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Luminescence-detected phase transitions in lanthanide-containing liquid crystals

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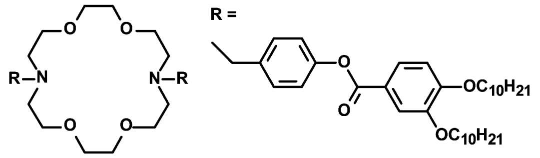
Complexes between lanthanide nitrates and a pro-mesogenic 18-membered diaza-substituted coronand are luminescent both as powders and liquid crystals (between 87 and 195 °C), and the phase transitions are detected by monitoring luminescence intensity and lifetime.

Liquid crystals are the main components of new-generation cost-saving colour displays and a great deal of research effort has been devoted to their development during the last two decades.[1] One disadvantage of these devices is their relatively low brightness, due to the use of polarisers and colour filters, and one way to overcome this shortcoming is the design of luminescent liquid crystals. While it is rather easy to find either photoluminescent sheets acting as filters or, even, organic-based luminescent liquid crystals, these materials display a broad-band, and usually blue, emission which is of little use in this context. On the other hand cathode-ray tubes rely on trichromatic phosphors emitting narrow bands in three basic colours, blue, green and red, and so do energy-saving luminescent lamps and tubes. Most of these phosphors contain rare-earth ions, Eu^{II} (blue), Tb^{III} (green) and Eu^{III} (red). Henceforth the idea of introducing lanthanide ions in mesogenic phases. Metallomesogens are relatively new in the area of liquid crystals and they combine the properties of a liquid crystalline phase with the optical and magnetic properties of the metal ions they incorporate. The first liquid crystalline phase containing Ln^{III} ions was reported by Piechocki.[2] Initially, it was thought that introducing bulky spherical ions in potentially mesogenic compounds could disrupt the required order to produce mesophases, but it turned out that many lanthanide-containing systems are amenable to form liquid crystalline phases, as reported in a recent comprehensive review article.[3]

Basically, there are two ways of designing luminescent lanthanide-containing mesophases. The first, historical, one is the introduction of highly luminescent complexes into known liquid crystalline phases and successful attempts with β-diketonates have been reported.[4–7] The other one is the synthesis of luminescent complexes displaying mesogenic properties.[8,9] Metal-centred luminescent properties, particularly those of Eu^{III}, have been taken advantage of to probe, at very low temperature, the degree of disorder around the metal ion in metastable liquid crystals based on europium laurate,[8] and to determine the second-rank crystal-field parameter through analysis of the $^5D_0 \rightarrow {}^7F_1$ transition in order to assess the magnetic anisotropy of europium-containing metallomesogens.[10,11] Here we present a new mesogenic class of luminescent lanthanide complexes built from a substituted diaza-18-crown-6 macrocyclic ligand, and we show, for the first time, how luminescence intensity and lifetime can be used to monitor the transitions from crystalline to liquid crystalline phases and *vice-versa*.

Synthetic macrocycles are selective and versatile ligands for the complexation of trivalent lanthanide ions. With one exception where a steroid-substituted benzo-15-crown-5 ether has been reacted with lanthanide nitrates to yield highly viscous liquid crystalline phases,[12] these ligands have not been investigated for the production of lanthanide-containing metallomesogens. Owing to the much better complexation ability of diaza-substituted crown ethers *versus* the all-ether ligands,[13] we have chosen a diaza-18-crown-6, or (2.2), framework onto which mesogenic pendant arms have been grafted. Ligand L (see below) has been obtained according to a classical synthetic route in which the brominated arms are reacted with (2.2).†



Complexes with formula $[Ln(NO_3)_3L]\cdot solv$ (Eu: solv = 0.25 H_2O; Tb: 1thf) are obtained by refluxing a solution of $Ln(NO_3)_3\cdot nH_2O$ in acetonitrile or thf, to which is added a solution of L in methylene chloride.‡

Thermal (TG and DSC, see Table 1) and polarized light microscopy (PLM) analyses of the ligand reveal a standard non-mesogenic behaviour with isotropisation occurring at 85 °C. On the other hand, the Eu^{III} complex is clearly mesogenic. The first heating reveals loss of 0.25 H_2O per molecule and: (i) a Cr → LC first order transition at 87 °C with a 25 °C hysteresis, (ii) a second exothermic and irreversible transformation at 124 °C which could correspond to a second order transition with partial disorganisation of the mesogenic phase and, (iii) isotropisation at 195–198 °C, immediately followed by decomposition. When temperatures higher than 170 °C are avoided, the sample shows perfect reversibility, except for the transition at 124 °C which is no longer seen. PLM photographs (Fig. 1) display a birefringent fine texture with very small Schlieren's patterns. The latter texture corresponds neither to a nematic nor to a smectic A phase and its detailed characterization by X-ray diffraction measurements is in progress.

The Eu^{III} complex has been analysed at low temperature by high-resolution laser-excited luminescence to probe the metal ion environment. Excitation spectra of the non-degenerate $^5D_0 \leftarrow {}^7F_0$ transition at 10 K evidence two components at 17268 (site I) and ≈ 17245 cm^{-1} (site II). Upon selective excitation, slightly different emission spectra are obtained which are dominated by the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition and which point, as expected, to a low symmetry around the Eu^{III} ion. Population analysis performed on the magnetic dipole $^5D_0$

Table 1 Thermal analysis data for the ligand and its complexes

Compound	Transition	T/°C	ΔH/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}
L	Cr → I	85	99	275
EuL	Cr → LC[a]	86	20	56
	LC → I	199	—	—
TbL	Cr → LC[a]	88	19	53
	LC → I	n.a.	—	

[a] Liquid crystalline phase (possibly columnar).

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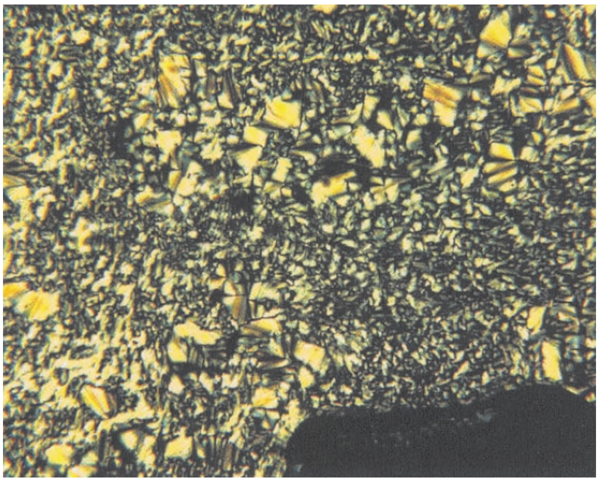

Fig. 1 Birefringent texture observed for [Eu(NO_3)$_3$L]·0.25H_2O at 110 °C (Leitz objective 20×/0.40, crossed polarizer and analyzer, Leica D300 F camera).

$\rightarrow {}^7F_1$ transition shows site I representing 79 ± 6% of the total Eu^{III} population. The lifetime, τ, of the Eu($^5D_0$) level amounts to about 1.1 ms for site I and 0.5 ms for site II. These data demonstrate that water interacts in the first coordination sphere of Eu^{III} in site II and are in line with the loss of 0.25 H_2O evidenced in TG analysis. With the idea of testing how the luminescence properties of the Eu^{III} ion vary during the phase transition, we have set up an experiment in which both the integrated intensity I of the $^5D_0 \rightarrow {}^7F_2$ transition and the Eu($^5D_0$) lifetime are monitored *versus* temperature.§ Generally speaking, increasing the temperature induces more non-radiative de-activation of the excited state and consequently, both the luminescence intensity and lifetime are expected to decrease according to an exponential law of the type $y = y_0 \cdot e^{-C/RT}$.[14] We have accordingly reported ln(τ/τ_{295}) and ln(I/I_{295}) *versus* the inverse of the absolute temperature on Fig. 2 to show that the phase transition intrinsically affects the luminescence parameters. Upon increasing the temperature, a sigmoid variation of both ratios is obtained. Crude mathematical analysis of these variations gives a transition temperature of 83 and 85 °C, respectively. Equally interesting are the variations obtained while cooling the sample. The ln(τ/τ_{295}) *vs.* 1/T curve closely follows the variation measured upon heating, while the ln(I/I_{295}) *vs.* 1/T curve is almost linear. Sigmoid analysis of both curve yields 86 and 81 °C, respectively, while DSC analyses display an hysteresis which is a function of the cooling rate (25 and 15 °C for rates equal to 5 and 0.1 °C min^{-1}, respectively). This apparent discrepancy probably arises from the fact that luminescence measurements are made at thermal equilibrium while DSC data are recorded dynamically. The low- and high-temperature values of τ and I are perfectly reproducible over tens of cycles.

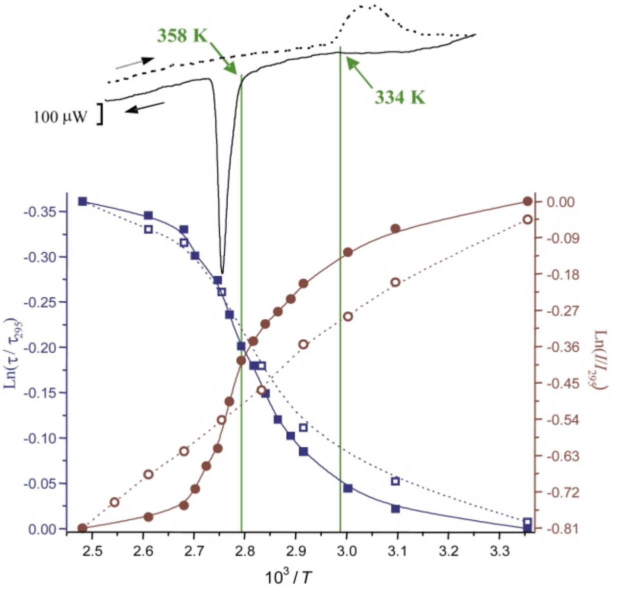

Fig. 2 Phase transition of [Eu(NO_3)$_3$L]·0.25H_2O. (Top) DSC traces at 5 °C min^{-1}. (Bottom) Integrated and corrected intensities of the Eu($^5D_0 \rightarrow {}^7F_2$) transition (right scale, ●: from 298 to 403 K, ○: from 403 to 298 K, excitation at 465.8 nm); lifetimes of the Eu($^5D_0$) excited level, analyzing wavelength set on the maximum of the $^5D_0 \rightarrow {}^7F_2$ transition (left scale, ■: from 298 to 403 K, □: from 403 to 298 K, excitation at 355 nm).

In conclusion, this study demonstrates that the well-known Eu^{III} luminescent probe[14] can be used to accurately monitor a crystalline-to-mesogenic phase transition and that substituted diaza-18-crown-6 coronands are suitable pro-mesogenic ligands, as are other macrocycles for other metallomesogens.[15] This opens the way to fascinating new developments in the field of lanthanide-containing liquid crystals.

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Notes and references

† Calc. for $C_{80}H_{126}N_2O_{12}$: C, 73.5; H, 9.7; N, 2.1. Found: C, 73.5; H, 9.8; N, 2.1%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.90 (m, 12H), 1.2–1.50 (m, 56H), 1.85 (m, 8H), 2.86 (m, 8H), 3.62–3.68 (m, 16 H), 3.72 (s, 8H), 4.08 (m, 8H), 6.92 (d, ^3J = 8 Hz, 2H), 7.13 (d, ^3J = 8 Hz, 4H), 7.28 (d, ^3J = 8 Hz, 4H), 7.67 (d, ^4J = 2 Hz, 2H), 7.80 (dd, ^3J = 8, ^4J = 2 Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 14.1 (primary C), 22.7–70.7 (secondary C), 111.9, 114.7, 121.4, 124.3, 129.7 (tertiary C), 121.7, 137.2, 148.6, 149.9, 153.7, 165.1 (quaternary C). ESI-MS (EtOH): *m/z* 1307.86 [L + H]$^+$ (calc. 1307.89) 30%, 654.87 [L + 2H]$^{2+}$ (calc. 654.95) 100%.

‡ Calc. for $C_{80}H_{126}N_5O_{21}Eu \cdot 0.25H_2O$: C, 58.2; H, 7.7; N, 4.2. Found: C, 58.0; H, 7.6; N, 4.2%. Calc. for $C_{80}H_{126}N_5O_{21}Tb \cdot THF$: C, 58.5; H, 7.8; N, 4.1. Found: C, 58.5; H, 8.1; N, 4.1%.

§ 2–3 mg of the Eu complex were deposited between two quartz Suprasil® windows and a film was formed by slight friction. The sample was placed into a specially designed thermostatted cell holder operating in the range 20 to 250 °C (±1 °C). A permanent stream of argon was flushed onto the sample to avoid decomposition. The sample was allowed to equilibrate for 10–15 min before each measurement.

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