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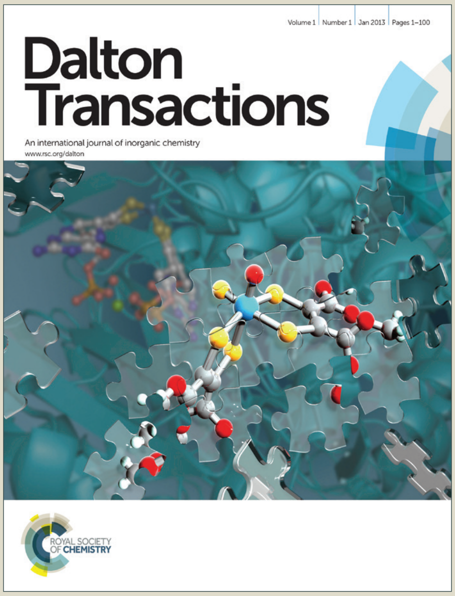

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A new class of thermotropic lanthanidomesogens: Eu(III) nitrate complexes with mesogenic 4-pyridone ligands

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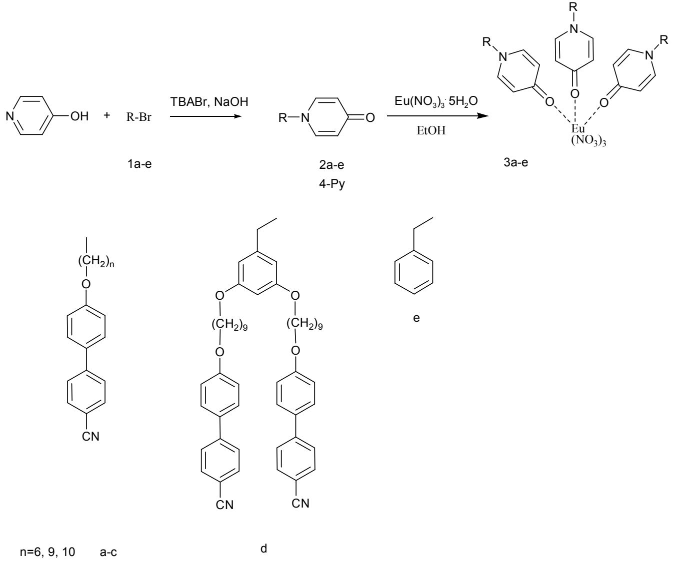
A new class of thermotropic lanthanidomesogens has been designed and prepared. They are based on 4-pyridone ligands that possess mesogenic cyanobiphenyl groups attached to the 4-pyridone unit via a flexible long alkyl spacer and show a very high thermal stability (decomposition temperatures near to 300°C). Depending on the alkyl length spacer, these complexes exhibit a SmA phase with transition temperatures influenced by the number of mesogenic group employed and spacer length.

Lanthanide-containing liquid crystals (lanthanidomesogens) are a special class of metallomesogens (metal-containing liquid crystals) that rapidly developed in the past three decades due to the unique photophysical properties of the lanthanide ions.[1] Their intense luminescence could be exploited in the construction of emissive LCDs. From the materials design point of view, the bulkiness of spherical Ln(III) ions as well as the large coordination numbers (typically eight or nine) made difficult their introduction in fluid LC phases. To address this issue, generally, two different approaches have been successfully used in the lanthanidomesogens design. The first well known concept is to decouple the mesogenic groups and the coordination units via long flexible alkyl spacers. In contrast, the other approach is to prepare high coordination number metallomesogens by increasing the number of long flexible alkyl chain attached to the coordinating unit. By applying the two concepts, several classes of lanthanidomesogens were developed and investigated such as: Schiff bases, β-diketonate, alkanoates, macrocyclic ligands (phtalocyanine, porphyrine, etc.), bis (benzimidazolyl) pyridine complexes, and these were extensively reviewed by several authors.[2-4] In order to make use of the interesting photophysical properties of the lanthanide ions, another concern in the lanthanidomesogens design is the use of well suitable ligands capable to form thermodynamically stable complexes with lanthanide ions as well as to play the antenna role, by absorbing light and transfer excitation energy to the emitting levels of the lanthanide ion. Starting from these premises we were interested to explore the possibility of using non-chelating *O*-donor ligands to prepare stable emissive lanthanidomesogens. We have designed new thermotropic lanthanidomesogens based on Eu(III) by using the first described concept, very efficient in promoting LC phases for different bulky entities, e.g. to decouple the mesogenic groups and the coordination units via a long flexible alkyl chain. In this case the coordination unit is represented by a 4-pyridone unit. 2- or 4-Pyridone derivatives have been known since long time as *O*-coordinated ligands in the coordination chemistry of lanthanides, including europium(III).[5] It is worth mentioning that 4-hydroxypyridine is a very appealing starting material as it can be either *N*- or *O*-alkylated with various bromide derivatives, yielding either 4-pyridones or *O*-substituted pyridines respectively.[6] The reaction of 4-hydroxypyridine with 4'-(ω-bromoalkyloxy)-4-cyanobiphenyl or benzyl bromide derivatives **1a**-**e** in THF, in the presence of NaOH and tetrabutylammonium bromide (TBABr) as phase transfer catalyst, gave the 4-pyridone derivative **2a**-**e**, as the main product in relatively high yield 56-88% (Scheme 1). Then, the Eu(III) complexes were relatively easy to prepare by reacting the 4-pyridone ligands with the $Eu(NO_3)_3 \cdot 5H_2O$ in hot ethanol

(Scheme 1). They were precipitated out of the solution and isolated as white solids in relatively good yields. The TG and elemental analysis show no crystallisation or coordination water molecules contained by these complexes.



Scheme 1. Preparation of 4-pyridone promesogenic ligands and their europium(III) nitrate complexes

Surprisingly, these thermotropic lantanidomesogens show a high thermal stability, with decomposition temperatures (T_{onset}) high above clearing temperatures, nearly 300°C (Table 1). To get further insights regarding their molecular structure we could successfully isolate single crystals of a parent complex containing 4-pyridone ligands without cyanobiphenyl mesogenic groups, previously prepared in a similar manner as the other Eu(III) complexes, by slow crystallisation from an acetonitrile solution. The colourless block crystals lose relatively fast their crystallization solvent molecules by exposure to air.

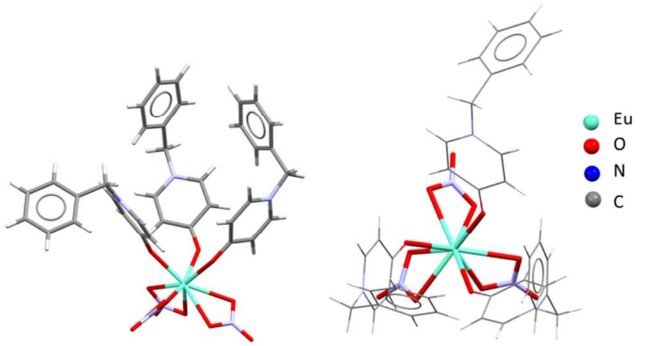


Fig. 1. Two different views of the molecular structure of complex **3e** (the solvent molecules were omitted for clarity).

The Eu(III) complex **3e** is nine-coordinate with six oxygen atoms from three bidentate coordinated nitrato groups while the coordination polyhedron is completed by other three oxygen atoms from the three 4-pyridone ligands. The full crystallographic details are given in ESI. We aimed to study two possible factors affecting the mesogenicity of these Eu(III) complexes. On the one hand the spacer chain length and on the other hand the number of mesogenic groups attached to the bulky metal centre.

The 4-pyridone ligands, except **2a**, show all a monotropic nematic phase. In the case of **3b**-**3d** complexes, a combination of differential scanning calorimetry (DSC), polarising optical microscopy (POM) and X-ray diffraction (XRD) indicate the formation of layered phases (SmA) and the absence of any crystallisation process on cooling the mesophase.

Table 1. Thermal parameters for 4-pyridone ligands and their Eu(III) complexes.

Compound	Transition[a]	T(°C)[b]	ΔH(kJ·mol^{-1})[c]	T_{onset}(°C)
2a	Cr-Iso	115	25.2	-
2b	Cr-Iso	128	49.7	-
	(g-N)	(9)	-	
	(N-Iso)	(76)	(1.2)	
2c	Cr-Iso	110	65.3	-
	(N-Iso)	(87)	(40.0)[d]	
	(Cr-N)	-	-	
2d	Cr-Iso	117	69.7	-
	(N-Iso)	(80)	(4.2)	
	(g-N)	(31)	-	
3a	Cr-Cr’	157	58.2	323
	Cr’-Iso	174	7.6	
	(g-Iso)	(65)	-	
3b	Cr-Iso	138	69.3	318
	(g-SmA)	(35)	-	
	(SmA-Iso)	(94)	(3.9)	
3c	g-SmA	23	-	319
	SmA-Iso	111	5.8	
3d	Cr-SmA	75	72.2	302
	SmA-Iso	100	15.2	
	(g-SmA)	(41)	-	

[a] g, N, SmA, Iso denotes glass transition, nematic, smectic A and isotropic phases, respectively. [b] The error on the transition temperatures is estimated to be ±0.5°. [c] The error on the enthalpy ΔH values was estimated to be ±0.5 kJ·mol^{-1}. [d] The combined enthalpy of the two transitions

The transitions observed by DSC, between mesophase and isotropic state are very sharp and well-defined. They are summarised in Table 1 together with the enthalpy associated to these processes. The temperature range of the liquid crystalline phase is greatly influenced by the spacer length and the number of cyanobiphenyl groups attached to the 4-pyridone unit. While the first heating run of **3b** and **3d** show a transition from a crystalline state to either isotropic state or LC phase respectively, the following heating-cooling cycles show only a glass transition to LC phase without any sign of crystallisation. The following heating-cooling cycles are perfectly reproducible and show only one peak corresponding to SmA-Iso transition and the glass transition in the same interval. No doubt, it is clear that a minimum spacer length is required in order to generate LC properties. For example, the Eu(III) complex with 6 carbon atoms, **3a**, has the highest melting point and does not show any mesogenic behaviour. It is interesting to note here that the related 4-pyridone ligand, **2a**, is non-mesomorphic as well. Cooling its isotropic phase from 175°C down to room temperature resulted in a glassy phase around 65°C. In contrast, higher number of carbon atoms (nine or ten) seems to be enough for the LC phase stabilisation with highest clearing temperature found for **3c** (111°C). In order to gain a better understanding of the LC phase nature the mesophase type was identified by variable-temperature XRD measurements. The XRD patterns of all the mesomorphic Eu(III) complexes **3b**-**3d** show two distinct sharp diffraction peaks in the low-angle region, in the 1:2 ratio, assigned to d_{001} and d_{002}, which is characteristic of a 1D lamellar ordering (Fig. 2). Another broad peak was found around 4.1-4.4Å assigned to the molten alkyl chain which confirms the fluid like nature of the mesophase. The layer thickness calculated was found to be weakly temperature-dependent suggesting a SmA phase. This is consistent with the POM observations, where a focal-conical fan shape texture was evidenced for all three mesomorphic Eu(III) complexes **3b**-**3d** (Fig. 2). Molecular calculations based on an all-trans extended model and taking into account the ligand arrangement around the metal centre as deduced for **3e**, suggested a monolayer arrangement, most probably in a head-to-tail fashion and a very weak interdigitation for complexes **3b**-3**d**.

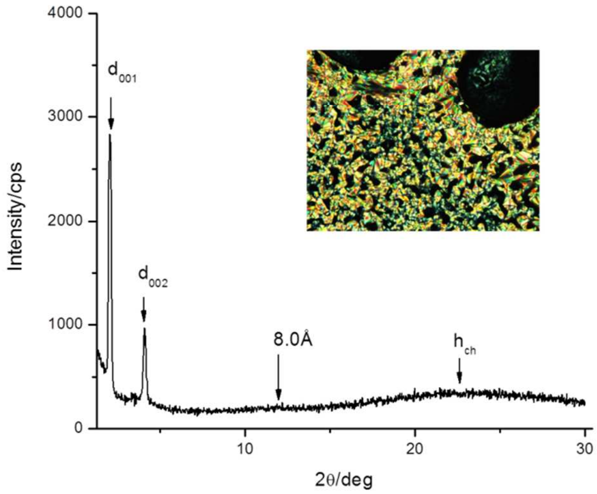


Fig. 2. XRD powder pattern for complex **3c** recorded at 70°C (inset microscope picture taken at 75°C and the tentative packing model within mesophase)

Interestingly, the XRD patterns of **3b**-**3d** show an additional broad and diffuse peak around 8.0Å which can be correlated with some additional organisation within layers, most probably with lateral distances between neighbouring molecules (the shortest Eu-Eu interaction in solid-state was found to be 8.7Å). The measured photoluminescence spectra of **3a-e** in solid-state at room temperature have shown the typical Eu(III) luminescence peaks associated to the $^5D_0 \rightarrow {}^7F_J$ (J=0-4) transitions (Fig. S18, ESI). Photoluminescence decay curves show single decay times with characteristic times ranging from 0.57 to 0.80ms, very similar to other reported Eu(III) complexes.[7] According to the structure of the **3e** complex the local symmetry expected for the Eu(III) ion is C_3. For **3c** and **3d** the $^5D_0 \rightarrow {}^7F_0$ luminescence transition (at 578nm) consists of one only peak, which gives a strong indication that all the Eu(III) ions occupy only one site with one of the C_s, C_n or C_{nv} symmetries.[8] For **3c** the $^5D_0 \rightarrow {}^7F_1$ band shows a crystal field structure (three peaks at 587, 591, 595nm) consistent with a low site symmetry of the Eu(III) ion, C_{2v} or even lower;[8] this structure has not been observed for **3d** sample. The $^5D_0 \rightarrow {}^7F_0$ luminescence single peak (at 578nm) is much weaker in the emission spectra of **3a** and **3b** that suggests a slight change (distortion) of the local symmetry compared to **3c**. Moreover, the luminescence spectra recorded at different temperatures, on heating from the glassy state or cooling from the isotropic state, after a previous heating-cooling cycle treatment of the sample, show a strong emission intensity discontinuity at the isotropic-SmA transition, as found for other mesogenic Eu(III) complexes, being a good indicative of phase transition (Fig. S20, ESI). Photoluminescence measurements and group-theoretical arguments have indicated that the addition of the mesogenic groups as well as the alkyl chain spacers have changed the local symmetry of the Eu(III)-ions for **3e** (C_3) but they have a weak influence on the photoluminescence decay times.

Conclusions

It has been shown that it is possible to design high thermally stable lanthanidomesogens based on a totally new class of monodentate mesogenic ligands, 4-pyridones derivatives, which can be very easily functionalized in order to tailor the LC properties. We aim to extend further this study to some other lanthanide ions in order to evaluate their influence on the mesogenic properties as well as to make use of their photophysical properties for various applications.

Notes and references

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† Electronic Supplementary Information (ESI) available: [synthesis details, crystallographic data, DSC traces, XRD patterns, luminescence spectra and POM pictures]. See DOI: 10.1039/c000000x/

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