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Preliminary communication

Luminescent lanthanide complexes with liquid crystalline properties

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Lewis-base adducts of tris(β-diketonato)lanthanide(III) complexes were prepared, where the β-diketone is *para*-alkoxy-substituted 1,3-diphenyl-1,3-propanedione. These compounds are the first examples of liquid crystalline lanthanide complexes in which the mesomorphism is introduced via a β-diketonate ligand. Depending on the type of the Lewis base, the metallomesogens exhibit a monotropic smectic A or a monotropic highly ordered smectic phase. Intense photoluminescence was observed for the europium(III) complexes at room temperature.

Although β-diketones have often been used in the design of new types of metal-containing liquid crystals (*metallomesogens*) [1], attempts to prepare mesomorphic lanthanide β-diketonates have known only limited success so far [2]. Because lanthanide β-diketonate complexes show an intense photoluminescence, such materials can be of interest for obtaining luminescent liquid crystals. Binnemans and Lodewyckx studied bis-adducts of [Ln(dbm)$_3$] complexes (Hdbm = 1,3-diphenyl-1,3-propanedione) with a salicylaldimine Schiff's base [3]. The adducts exibited a monotropic smectic A phase, but in their structure NH bonds are present which decrease the luminescence quantum yield. Hapiot and Boyaval studied 1:1 adducts of [Ln(tta)$_3$] (Htta = 2-thenoyl-trifluoroacetylacetone) and cholesteryl nonanoate or cholesteryl tetradecanoate [4]. These compounds themselves were not mesomorphic, but the corresponding europium(III) complex dissolved in a cholesteric liquid crystal mixture showed an intense red photoluminescence [5].

In this preliminary communication, we present the first examples of liquid crystalline lanthanide complexes in which the mesomorphism is introduced via a β-diketonate ligand. Three different types of Lewis-base adducts of tris(β-diketonato) lanthanide(III) complexes were prepared (figure 1), where the β-diketone is *para*-alkoxy-substituted 1,3-diphenyl-1,3-propanedione, and the Lewis base is either 1,10-phenanthroline (**1a**,**b**), 2,2′-bipyridine (**2a**) or an alkanoyloxy 4,4′-disubstituted 2,2′-bipyridine (**2b**,**c**). As the central lanthanide ions, europium(III) and terbium(III) was chosen.

The β-diketone ligand was synthesized by Claisen condensation of the ethyl ester of 4-tetradecyloxybenzoic acid and 4-tetradecyloxyacetophenone with sodium hydride as the base, according to a literature method [6]. The tetradecyl diester of 2,2′-bipyridine-4,4′-dicarboxylic acid was obtained by esterification of 2,2′-bipyridine-4,4′-dicarboxylic acid and 1-tetradecanol using the acid

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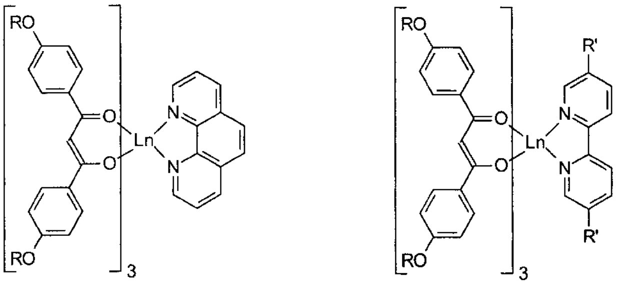

R = $C_{14}H_{29}$
1a: Ln = Tb
1b: Ln = Eu

R = $C_{14}H_{29}$
2a: Ln = Eu, R' = H
2b: Ln = Eu, R' = $CO(O)C_{11}H_{23}$
2c: Ln = Tb, R' = $CO(O)C_{11}H_{23}$

Figure 1. Schematic structure of the Lewis-base adducts of the tris(β-diketonato)lanthanide(III) complexes with 1,10-phenanthroline (**1a**, **1b**) or 2,2′-bipyridines (**2a**–**c**).

chloride (obtained from the acid with thionyl chloride). The lanthanide coordination compounds **1**, **2** were prepared by mixing the β-diketone (3 eq.), sodium hydroxide (3 eq.) and the Lewis base (1 eq.) in absolute ethanol at 70–75°C, followed by dropwise addition of an ethanolic solution of the lanthanide chloride salt. After cooling, the precipitate was filtered off, washed with cold absolute ethanol and dried *in vacuo*. Yields varied between 70 and 80%. All lanthanide compounds gave satisfactory CHN elemental analysis results. For instance, for compound **1b** calc. for $C_{145}H_{213}EuN_2O_{12}$ (2328.21) C 74.80, H 9.22, N 1.20; found C 76.64, H 9.27, N 1.12%.

Elemental analyses were obtained on a CE-Instrument EA-1110 elemental analyser. Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller. DSC traces were recorded with a Mettler-Toledo DSC821e module. Luminescence spectra were recorded at ambient temperature and a liquid nitrogen temperature (77 K) using an Edinburgh Instruments FS900 Steady State Spectrofluorimeter, with a bath cryostat (Oxford Instruments).

All the complexes were mesomorphic. The complexes melt without formation of a mesophase upon heating, but upon cooling a monotropic smectic A (compounds **1a**, **1b**, **2a**) or a monotropic highly ordered smectic phase (compounds **2b** and **2c**) was formed. The phase transitions were studied by polarizing optical microscopy and by differential scanning calorimetry (DSC). For the smectic A phase, typical bâtonnets which coalesced to a fan-shaped texture were observed. For the highly ordered smectic phase, granular patterns or mosaic textures were observed; sometimes concentric arcs were also seen. This behaviour is reminiscent of that of the crystal G phase [7]. However, until detailed XRD studies have been made, we will label this mesophase smectic X (SmX). The fluidity of the mesophase was checked by pressing with the point of a needle on the cover glass of the microscope preparation. The transition temperatures are summarized in the table. The DSC thermogram of compound **1b** is shown in figure 2. In contrast to the previously described Schiff's base adducts of [Ln(dbm)$_3$], the mesophases formed by the compounds presented here have a higher stability, i.e. they exist over a wider temperature range and have less tendency to crystallize [3]. The mesophases could be vitrified by fast cooling.

The molecular anisometry necessary for obtaining a mesophase is not directly evident from the published crystal structures of Lewis-base adducts of tris-(β-diketonato)lanthanide(III) complexes [8]. However, it is well known that a smectic A mesophase is formed by many types of unconventional mesogens, not only by the classical rod-like types [9]. The existence of a smectic A or a smectic X phase reveals that in the

Table. Mesomorphic behaviour of the tris(β-diketonato)-lanthanide(III) complexes. Cr = crystalline solid; SmA = smectic A phase; SmX = smectic X phase; I = isotropic liquid.

Compound	Ln(III)	*R′*	Transition temperatures/°C
1a	Tb	—	Cr 145 [120 SmA] I
1b	Eu	—	Cr 155 [138 SmA] I
2a	Eu	H	Cr 133 [115 SmA] I
2b	Eu	$CO(O)C_{11}H_{23}$	Cr 166 [149 SmX] I
2c	Tb	$CO(O)C_{11}H_{23}$	Cr 162 [143 SmX] I

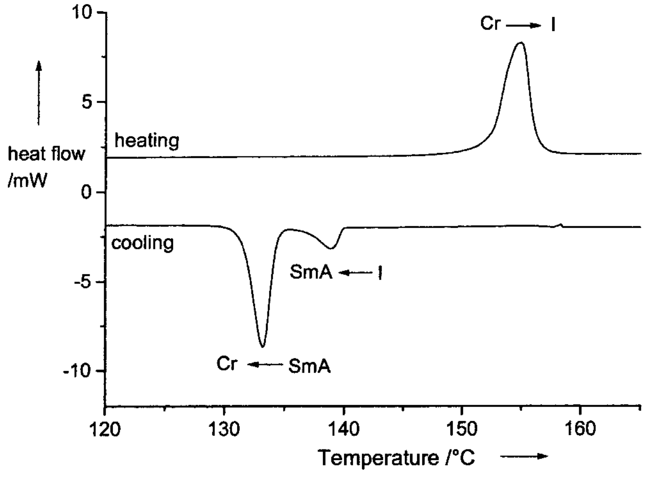

Figure 2. DSC-trace of compound **1b**. Endothermic peaks point upwards. The enthalpy change for the Cr → I transition at 155°C is 27.39 kJ mol^{-1} and the enthalpy change of the I → SmA transition at 138°C is 3.79 kJ mol^{-1}.

mesophase an organized layer structure must be present (with additional order within and possibly between the layers for the smectic X phase). Although we could not obtain single crystals of our complexes with long alkoxy chains, molecular modelling simulations showed that it is possible to obtain layer-like structures with this type of complex by folding the chains towards each other so thay they are more or less parallel. The longer the alkyl chain, the more easily the chains can fold together to form layers. The coordination number of the lanthanide ion in all the complexes is eight, and the coordination polyhedron can be described most probably as a distorted dodecahedron or a distorted square antiprism.

Upon irradiation by ultraviolet light, all the europium(III) complexes showed an intense red photoluminescence in the solid state at room temperature (figure 3). This solid state can be either a powder sample or a vitrified mesophase. The luminescence spectrum is a typical europium(III) emission spectrum of transitions between the $^5D_0$ excited state and different *J*-levels of the ground term ^7F. The most intense transition in the spectrum is the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 13.5/1. The splitting of the $^7F_1$ level into three crystal-field levels indicates that the symmetry of the europium(III) site is orthorhombic or lower. From the equidistance of the crystal-field levels of the $^7F_1$ multiplet, one can conclude that the real coordination polyhedron of the europium ion is far distorted from the ideal dodecahedron or ideal square antiprism.

In conclusion, a new type of luminescent lanthanide complex with liquid crystalline behaviour has been obtained. In this work we show that the properties of liquid crystallinity and intense luminescence can be combined in one and the same compound. The β-diketones are very versatile ligands that can be used to obtain high coordination number metallomesogens. After it was shown by Swager and coworkers that tris(β-diketonato)-iron(III) and tetrakis(β-diketonato)zirconium(IV) complexes exhibit liquid crystallinity [10, 11], we have extended this work to the elements of the lanthanide series [2, 12]. Our compounds form a new class of metallomesogen with coordination number eight. Research is in progress to reduce the transition temperatures, to optimize the luminescence behaviour, and to characterize the smectic X phase.

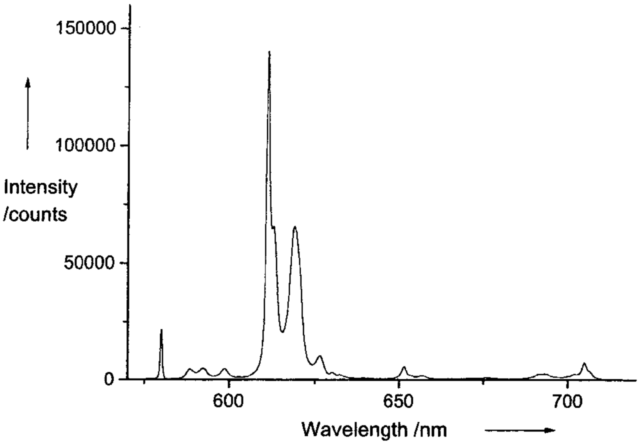

Figure 3. Photoluminescence spectrum of europium(III) compound **2a** at room temperature. The excitation wavelength was 390 nm. All transitions start from the $^5D_0$ level.

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