



Controlled polarized luminescence of smectic lanthanide complexes



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ABSTRACT

A new series of β -diketonate lanthanide adducts with 5,5'-di(heptadecyl)-2,2'-bipyridine, showing a smectic thermotropic mesomorphism, has been synthesized. The peculiar thermodynamic dependence of the phase transitions with the lanthanide ion is described, and the liquid crystalline properties of the series have been analyzed by SAXS. The luminescence in the solid state for the Eu(III), Sm(III), Yb(III), Er(III) and Nd(III) adducts was investigated. The enhancement of the luminescence by the orientation of the LC domains through film shear deformation is demonstrated.

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1. Introduction

In the last decade, there has been considerable activity in the field of lanthanide-containing liquid crystals (*lanthanidomesogens*) [1–4]. Due to their high coordination number ($6 \leq CN \leq 12$), the resulting coordination polyhedra in 4f lanthanide complexes exhibit different geometries than from those traditionally obtained with transition 3d and 4d metal complexes [5], with, for example, nine-coordinate tricapped trigonal prismatic or eight-coordinate square antiprismatic ligand arrangements around the metal ion [6]. These rather unpredictable three-dimensional coordination geometries render therefore trivalent lanthanide metal ions more challenging for introduction into thermotropic liquid crystals than transition metal ions [7,8], but give several new attractive opportunities for investigating new structure-mesomorphism relationships [1–4]. The most successful strategy in designing lanthanidomesogens has mainly consisted in coordinating various mesomorphic ligands, wrapping the trivalent ion [1], but

mesomorphism could also be induced by the right combination of non-mesomorphic ligands. The first examples of the emergence of liquid crystallinity in lanthanidomesogens with non-mesomorphic ligand were found with lanthanide Schiff's base complexes with the stoichiometry $[\text{Ln}(\text{LH})_2\text{LX}_2]$ (where LH is the non mesomorphic salicylaldehyde Schiff's base, and X is the counterion) and with some Lewis base adduct of tris(β -diketonates ($[\text{La}(\text{dk})_3\text{LH}]$)), respectively [9,10].

Some elements of the lanthanide series show strong luminescence [11–15] and interesting magnetic properties [16,17]. The emission observed for these materials is metal-centered between energy levels within the 4f shell of the trivalent lanthanide ion. Organic ligands coordinating a lanthanide ion (for example, β -diketonates, Lewis bases) ensure the transfer of the excitation energy onto the emissive ion (antenna effect) [18,19]. The two main advantages of luminescence in trivalent lanthanide ions is: i) their narrow emission lines of a high color purity [20–22], and ii) the facile tuning of the emission wavelength by the proper choice of the lanthanide ion: red emission is obtained with Eu(III), green emission with Tb(III), blue emission with Tm(III), orange emission with Sm(III), and near-infrared emission with Nd(III), Er(III) and Yb(III) ions [23]. The mesomorphic properties within this family of compounds bring the anisotropy of the magnetic properties [24–29], allowing controlled orientation of magnetic domains, and optical properties, allowing one to create luminescent materials that emit

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polarized monochromatic light [30,31] in the mesophases. Several other studies on the influence of the luminescence as a function of the orientation of the liquid crystals [32–34], LC polymers [35,36], zeolites [37–40] and lanthanide complexes [41–44] have been reported and proved very promising to control luminescence properties. Thus, the synthesis and understanding behavior of liquid crystals based on lanthanide ions are timely and pressing challenges for the development of new optoelectronic materials.

This study presents the synthesis of a new series of β -diketonate lanthanide adducts with 5,5'-di(heptadecyl)-2,2'-bipyridine (bpy₁₇₋₁₇) as co-ligand, which shows thermotropic mesomorphism with a rare example of smectic phases induction. Only few successful samples of complexes with Lewis bases are known [45–49]. The peculiar thermodynamic dependence of the phase transitions with the lanthanide ions is described, and the liquid crystalline properties of the series have been analyzed by DSC, POM and SAXS. The luminescence in the solid state was investigated for the Eu(III), Sm(III), Yb(III), Er(III) and Nd(III) adducts, and enhancement of the luminescence could be achieved by the orientation of the LC domains through film shear deformation.

2. Results and discussion

2.1. Synthesis and characterization

An almost complete series of lanthanidomesogens, namely tris-[1-(4-(4-pentylcyclohexyl)phenyl)-3-(thiophen-2-yl)propane-1,3-dionato]-[5,5'-di(heptadecyl)-2,2'-bipyridine] lanthanum, of the type [Ln(CPDK_{5-Th})₃(bpy₁₇₋₁₇)], where Ln = La(III), Nd(III), Eu(III), Sm(III), Gd(III), Tb(III), Ho(III), Er(III), Yb(III), Lu(III), has been synthesized (Fig. 1).

The synthesis of both the ligands is known and has already been reported elsewhere [41,43]. The general method for the synthesis of the lanthanide complexes [Ln(CPDK_{5-Th})₃(bpy₁₇₋₁₇)] is straightforward and briefly described now: 0.115 g (0.3 mmol) of 1-(4-(4-pentylcyclohexyl)phenyl)-3-(thiophen-2-yl)propane-1,3-dione (CPDK_{5-Th}), 0.063 g (0.1 mmol) of 5,5'-diheptadecyl-2,2'-bipyridine (bpy₁₇₋₁₇) and 0.017 g (0.3 mmol) of KOH were dissolved in 20 mL of 96% ethanol, and the mixture stirred and heated to 70 °C. Then, was followed the drop wise addition of a solution of La(III)Cl₃·5H₂O 0.034 g (0.1 mmol) in ethanol (1.5 mL), and the mixture stirred for 5 more min at 70 °C. The precipitate was filtered, purified in ethanol and then dried in vacuum above P₂O₅. All the complexes were fully characterized by elemental analysis and mass spectrometry, and the ¹H NMR was performed for the La(III) complex.

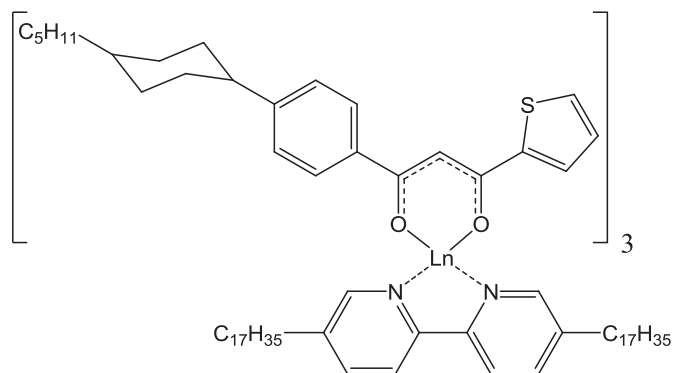


Fig. 1. Structure of the lanthanide(III) β -diketonate complexes [Ln(CPDK_{5-Th})₃(bpy₁₇₋₁₇)], with Ln = La(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Ho(III), Er(III), Yb(III), Lu(III).

La(CPDK_{5-Th})₃bpy₁₇₋₁₇: Yield: 0.132 g (69%). ¹H NMR (400 MHz, CDCl₃): δ 8.45–8.53 (m, 2H, Pyr H³), 8.23–8.27 (m, 2H, Pyr H⁶), 7.86–7.90 (m, 6H, Ph), 7.78–7.84 (m, 3H, Th), 7.61–7.65 (m, 3H, Th), 7.57–7.60 (m, 2H, Pyr H⁴), 7.28–7.36 (m, 6H, Ph), 7.15–7.18 (m, 3H, Th), 6.42–6.55 (m, 3H, CH-CO); 2.61–2.67 (m, 4H, CH₂-Pyr), 2.49–2.59 (m, 3H, CH-Ph), 1.88–1.95 (m, 12H, C₆H₁₀), 0.99–1.67 (m, 99H, CH₂, C₆H₁₀), 0.83–0.96 (m, 15H, CH₃). Found (%): C, 71.02; H, 9.00; N, 1.34; S, 5.10; La, 7.10. C₁₁₆H₁₆₃N₂O₆S₃La. Calcd (%): C, 72.69; H, 8.57; N, 1.46; S, 5.02; La, 7.25. ESI-MS (*m/z*): 1939.4 (M + Na)⁺. **Nd(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.135 g (70%). Found (%): C, 72.03; H, 8.98; N, 1.40; S, 5.02; Nd, 7.50. C₁₁₆H₁₆₃N₂O₆S₃Nd. Calcd (%): C, 72.49; H, 8.55; N, 1.46; S, 5.00; Nd, 7.50. ESI-MS (*m/z*): 1944.7 (M + Na)⁺. **Sm(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.132 g (68%). Found (%): C, 71.71; H, 9.05; N, 1.45; S, 4.80; Sm, 7.50. C₁₁₆H₁₆₃N₂O₆S₃Sm. Calcd (%): C, 72.26; H, 8.52; N, 1.45; S, 4.99; Sm, 7.80. ESI-MS (*m/z*): 1950.8 (M + Na)⁺. **Eu(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.130 g (67%). Found (%): C, 71.66; H, 8.99; N, 1.35; S, 4.75; Eu, 7.75. C₁₁₆H₁₆₃N₂O₆S₃Eu. Calcd (%): C, 72.20; H, 8.51; N, 1.45; S, 4.98; Eu, 7.87. ESI-MS (*m/z*): 1952.4 (M + Na)⁺. **Gd(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.129 g (66%). Found (%): C, 71.55; H, 8.98; N, 1.35; S, 4.76; Gd, 8.00. C₁₁₆H₁₆₃N₂O₆S₃Gd. Calcd (%): C, 72.00; H, 8.49; N, 1.45; S, 4.97; Gd, 8.13. ESI-MS (*m/z*): 1957.7 (M + Na)⁺. **Tb(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.132 g (70%). Found (%): C, 71.45; H, 9.02; N, 1.28; S, 4.73; Tb, 8.05. C₁₁₆H₁₆₃N₂O₆S₃Tb. Calcd (%): C, 71.94; H, 8.48; N, 1.45; S, 4.97; Tb, 8.21. ESI-MS (*m/z*): 1959.4 (M + Na)⁺. **Ho(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.125 g (64%). Found (%): C, 71.26; H, 8.88; N, 1.31; S, 4.65; Ho, 8.15. C₁₁₆H₁₆₃N₂O₆S₃Ho. Calcd (%): C, 71.72; H, 8.46; N, 1.44; S, 4.95; Ho, 8.49. ESI-MS (*m/z*): 1965.4 (M + Na)⁺. **Er(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.122 g (63%). Found (%): C, 71.15; H, 8.95; N, 1.26; S, 4.75; Er, 8.50. C₁₁₆H₁₆₃N₂O₆S₃Er. Calcd (%): C, 71.63; H, 8.45; N, 1.44; S, 4.95; Er, 8.60. ESI-MS (*m/z*): 1967.7 (M + Na)⁺. **Yb(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.125 g (64%). Found (%): C, 71.00; H, 8.86; N, 1.19; S, 4.70; Yb, 8.55. C₁₁₆H₁₆₃N₂O₆S₃Yb. Calcd (%): C, 71.42; H, 8.42; N, 1.44; S, 4.93; Yb, 8.87. ESI-MS (*m/z*): 1973.5 (M + Na)⁺. **Lu(CPDK_{5-Th})₃bpy₁₇₋₁₇:** Yield: 0.127 g (65%). Found (%): C, 70.88; H, 8.82; N, 1.23; S, 4.66; Lu, 8.75. C₁₁₆H₁₆₃N₂O₆S₃Lu. Calcd (%): C, 71.35; H, 8.41; N, 1.43; S, 4.93; Lu, 8.96. ESI-MS (*m/z*): 1975.4 (M + Na)⁺.

2.2. Mesomorphism

All lanthanide complexes are mesomorphic, despite that both β -diketonate 1-(4-(4-pentylcyclohexyl)phenyl)-3-(thiophen-2-yl)propane-1,3-dione [50] and 5,5'-diheptadecyl-2,2'-bipyridine [51,52] ligands are themselves not liquid-crystalline, melting directly into the isotropic liquid at 104 °C and 82 °C, respectively. The thermal behavior of the Ln(III) adducts is summarized in Table S1 and in the phase diagram shown in Fig. 2. The melting points (determined during the first heating treatment) of the complexes do not depend much on the size of the Ln(III) ion, but still nevertheless show a zig-zag variation along the series from the neodymium up to the erbium derivatives, oscillating between ca 140–160 °C. The clearing temperatures of the Ln(III) complexes (Table S1, determined on further heating) do not depend on the size of the ion, and they isotropize at around ca 222–236 °C, except for the La(III) derivative, which clears at 200 °C. The mesophase was identified as an untitled smectic phase, smectic A (SmA) for all but the La(III) adduct, which instead shows likely the more ordered smectic B phase (SmB), as deduced from hot-stage polarizing optical microscopy. Upon cooling from the isotropic melt, typical bâtonnets of SmA-like phase were formed (Fig. 3). These bâtonnets coalesce to give rise to a fan-shaped focal conic textures (Fig. 4). On further cooling below room temperature, the Ln(III) complexes do not crystallize but the mesophase freezes into a glass. No decomposition of the samples

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