

Letters to the Editor

Liquid-crystalline complex of Eu^{III} β -diketonate with 5,5'-di(heptadecyl)-2,2'-bipyridine

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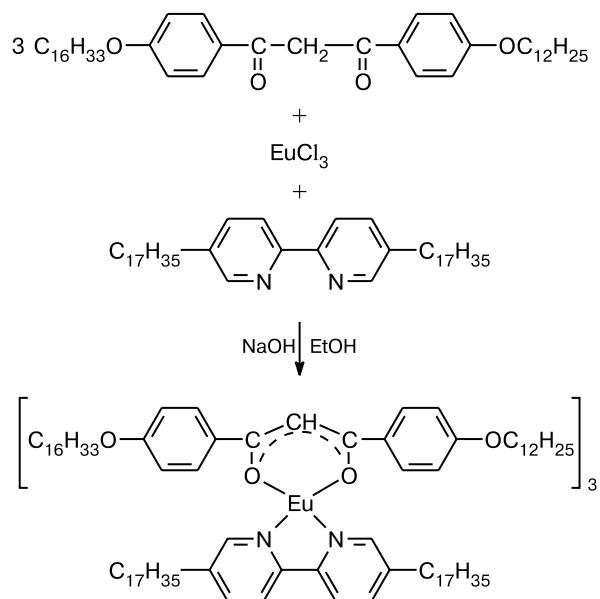
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Complexes of lanthanide β -diketonates with Lewis bases are used as emitters and transmitters in organic light-emitting diodes. In compounds of this class, the excitation energy transfer to an emitting lanthanide ion (antenna effect) is provided by ligands (β -diketones, Lewis bases) coordinated with the lanthanide ion.¹ In heterogeneous lanthanide-containing structures of the polymer–lanthanide salt type absorption (self-quenching) of radiation occurs, while in materials with an ordered organization of ions luminescence enhances considerably.² Therefore, self-organized liquid-crystalline compounds are considered^{3,4} promising for the creation of defectless optical media. This communication presents the synthesis of the anisometric adduct of europium β -diketonate with 5,5'-di(heptadecyl)-2,2'-bipyridine, which possesses liquid-crystalline properties (Scheme 1).

Complexes of lanthanide β -diketonates with Lewis bases are usually obtained in an aqueous-alcohol medium.⁵ However, a low solubility in water of the ligands used in this work forced us to perform the reaction in ethanol. The duration of the reaction was at most 10 min to prevent the formation of by-products.

Scheme 1



The compound synthesized was characterized by elemental analysis, thermography, and IR and luminescence spectra. The compound melts on heating to form a fan texture, which is seen with a polarization microscope. The temperatures of the crystal—mesophase and mesophase—isotropic liquid phase transitions are 95 and 130 °C, respectively. After UV irradiation, the solid Eu complex exhibits intense red photoluminescence at room temperature. Transitions between the ⁵D₀ excited state and different J levels in the ⁷F region (at 577, 582, 595, 616, and 652 nm) with a ratio of intensities $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ of 16 : 1 are observed in the spectrum.

The texture and temperatures of phase transitions were determined with a Boetius polarization microscope. IR spectra were recorded on a Bruker IFS66VIS spectrometer. Luminescence spectra were obtained in the 90° geometry on an automated optical spectrometer using an LGI-21 nitrogen pulse laser (wavelength 337 nm), a halogen incandescent lamp (working interval 350—800 nm), an MDR-23 monochromator, and an FEU-100 photodetector (sensitivity region 170—830 nm).

Tris[1-(4-dodecyloxyphenyl)-3-(4-hexadecyloxyphenyl)propane-1,3-dione]-[5,5'-di(heptadecyl)-2,2'-bipyridine]europium. A solution of EuCl₃·6H₂O (1.5 mL, 0.037 g, 0.1 mmol) in EtOH heated to 70 °C was added for 30 s at 70 °C to a solution of β-diketone⁶ (0.195 g, 0.3 mmol), bipyridine⁷ (0.032 g, 0.1 mmol), and NaOH (0.012 g, 0.3 mmol) in 96% EtOH (20 mL). A precipitate was formed immediately. The suspension was stirred for 10 min. The hot yellow finely dispersed precipitate was filtered off, washed with EtOH, and dried *in vacuo* over P₂O₅. The yield was 0.166 g (62%), m.p. 130 °C. Found (%):

C, 75.98; H, 10.28; N, 1.05. C₁₇₃H₂₇₉EuN₂O₁₂. Calculated (%): C, 76.08; H, 10.30; N, 1.03. IR (KBr), ν/cm⁻¹: 1609, 1588, 1470, 1435, 1257 (C=N, C=C, Py); 1541, 1435, 938 (C=O); 1394, 1377, 1021 (Me); 1219, 1129, 725, 422 (C₆H₄); 1176, 846, 705 (CH, Py).

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