

# Luminescent Langmuir–Blodgett film of a new amphiphilic $\text{Eu}^{3+}$ $\beta$ -diketonate

Luciano F. Gomes, Kleber T. de Oliveira, Cláudio R. Neri\*, Paulo C. de Sousa Filho, Marcos J. Dal Bianco, Ana P. Ramos, Maria E.D. Zaniquelli, Osvaldo A. Serra\*

*Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Avenida dos Bandeirantes, 3900, CEP 14040-901, Ribeirão Preto, SP, Brazil*

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## Abstract

This work reports on the synthesis and characterization of the ligand 3-hexadecylpentane-2,4-dione (Hhdacac) and its  $\text{Eu}^{3+}$  complexes  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$  and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$ , where phen and tta denote 1,10-phenanthroline and thenoyltrifluoroacetone, respectively. These new compounds present long carbon chains and their expected miscibility into non-polar ambients is confirmed by the emission spectra of  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  in hexane. Moreover, the amphiphilic properties of  $\text{Eu}(\text{hdacac})_6$  complexes allow the obtainment of thin luminescent films by the Langmuir–Blodgett technique. In both cases (solids and films), the typical antenna effect of  $\beta$ -diketonates is observed. The alluring characteristics of these compounds raise great interest in many fields of Materials Science, like photo- and electro-luminescent materials (mainly thin “organic” films), metal catalysts or probes in non-polar solutions, and Langmuir–Blodgett films of several compositions. For the characterization of these products, nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR), thermogravimetric analysis, elementary analyses (C, H), scanning electron microscopy (energy dispersive X-ray spectroscopy), absorption (UV–vis/FT–IR) and photoluminescence spectroscopies were used.

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## 1. Introduction

Europium (III)-containing complexes have attracted more and more attention due to their unique f–f electronic transitions, which result in narrow and intense emission bands via an effective intramolecular energy transfer from the ligands to the ion. This phenomenon, called the antenna effect [1–4], bypasses the weak absorption of free lanthanide ions and improves their luminescence yields. Among several types of ligands,  $\beta$ -diketonates (1,3-diketones) give rise to very attractive absorption bands not to mention their many other particular properties. The  $\beta$ -diketonates are known for being able to chelate with  $>60$  metals, for their high stabilities, they can be stored for a

long time, and for their miscibility in organic solvents (alcohol, ether, benzene, carbon tetrachloride, chloroform, xylene, and others) [5,6]. The complexation of rare-earth ions with these ligands have been widely studied in several aspects [7–12], and, therefore, these compounds have found numerous applications in optical devices (liquid crystal displays, “organic” light-emitting diodes, and chelate lasers) and in Analytical Chemistry (NMR shift reagents, chemical sensors, and stationary phases in gas chromatography), for example [7]. Moreover, some successfully fabricated and investigated  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ , and  $\text{Tb}^{3+}$  luminescent complexes with long aliphatic chains (on the carbonyl groups) and with amphiphilic behavior have been remarkable [13–15].

The development of optical devices requires the synthesis and characterization of luminescent compounds with different characteristics, and that can be processed, for example, in the form of solid films [13–19]. In this sense,

\*Corresponding authors. Tel.: +55 16 3602 3746/55 16 3602 4376; fax: +55 16 3602 4838.

E-mail address: [crneri@usp.br](mailto:crneri@usp.br) (C.R. Neri).

thin films containing europium complexes can be prepared by different methods, in particular by the Langmuir–Blodgett (LB) technique, which allows the formation of ordered thin films ranging from one molecule thick up to several nanometers (many layers). Photoluminescence studies of these films may disclose unusual features when compared to the characteristics of the complexes in solution, in the solid state, or in non-ordered films [20–23]. Moreover, there are different strategies that can be applied in consonance with the LB technique. Probably, the most used one is the introduction of a hydrophobic substituent in the compound of interest, which enables its spreading at the air/liquid interface [16,24,25]. It is equally possible to prepare Langmuir monolayers with a lipid that spreads easily in an aqueous subphase containing the ion of interest [17,18]. LB films of this type may be otherwise forced to exchange some ligands to obtain stronger luminescent signals [16]. The range of ligands for europium ions is wide and diversified, which means that different luminescent materials or different applications may be developed depending on the selected ligand.

In this work, we report the synthesis of 3-hexadecylpentane-2,4-dione (Hhdacac) and its  $\text{Eu}^{3+}$  complexes  $\text{Eu}(\text{hdacac})_3(\text{Hhdacac})_3 \cdot x\text{H}_2\text{O}$  (from now on we denote  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$ , assuming  $x \approx 2$ ),  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$ , and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  ( $\text{phen} = 1,10$ -phenanthroline,  $\text{tta} = \text{thenoyltrifluoroacetone}$ ). This peculiar  $\beta$ -diketone contains a substituent on the carbon between the two carbonyl groups, which allows a better distribution of this chelating agent around the ion. The structure of the synthesized ligand was confirmed by  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR). The compositions of the prepared  $\text{Eu}^{3+}$  complexes were elucidated by complexometric titration ( $\text{Eu}^{3+}/\text{edta}$ ), thermogravimetry (TGA), and FT-IR spectroscopy. UV-vis absorption and photoluminescence spectroscopy (emission, excitation, lifetimes, and quantum efficiencies) were also applied for the characterization of the complexes. Due to the particular physico-chemical properties of these compounds, they did not render good films when techniques like dip coating and spin coating were employed; so in this work, we report a methodology to prepare thin films from these compounds by applying the LB technique. The luminescence of the obtained films was also analyzed, and a comparison between the spectroscopic behavior of the solids and the films was made.

Due to their long aliphatic chains (amphiphilic character), the synthesized complexes are miscible in hydrophobic ambients, as shown by the emission spectra of  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  in hexane. Hence, these complexes, as well as those containing other rare-earth ions, may have potential use as catalysts or probes in non-polar ambients, as precursors for organic-inorganic photo- or electro-luminescent devices, and for LB films with many attractive characteristics.

## 2. Experimental

### 2.1. Apparatus

$^1\text{H}$  NMR spectra were acquired on a Brüker AVANCE 400 spectrometer. Measurements were carried out at room temperature ( $\sim 300$  K). Deuterated chloroform ( $\text{CDCl}_3$ ) was used as solvent and tetramethylsilane (TMS) as an internal reference.

TGA was carried out (Thermal analyst 2100-TA Instruments STD 2690-Simultaneous DTA-TGA) in synthetic air atmosphere, with a heating rate of  $10^\circ\text{C min}^{-1}$ . Elemental analysis (C, H) was performed in a Carlo Erba CE Instruments, EA 1110. The infrared spectra were recorded (Perkin-Elmer 502) from  $4000$  to  $400\text{ cm}^{-1}$  in KBr pellets. The absorption spectra were recorded on a HP Diode Array 8453A spectrophotometer. The emission and excitation spectra (of solids and films) were obtained at room temperature ( $\sim 300$  K), using a SPEX Triax 550 Fluorolog III spectrofluorometer. The recorded spectra were corrected for the lamp intensity and for the photomultiplier sensitivity by using the apparatus software. Luminescence lifetime measurements were carried out using a SPEX 1934D phosphorimeter, equipped with a pulsed xenon lamp. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDS) spectra of the films were acquired on a Zeiss EVO 50 scanning electron microscope with a 500 Digital Processing accessory (IXRF Systems).

### 2.2. Ligand, complex, and LB film preparation

#### 2.2.1. 3-Hexadecylpentane-2,4-dione (Hhdacac)

The synthesis of Hhdacac [26,27] (Fig. 1) was accomplished by mixing 1-iodohexadecane (Aldrich, 95%) (5.58 g, 15.0 mmol) and sodium acetylacetonate (prepared as described by Charles [28]) (1.46 g, 12.0 mmol) in methyl ethyl ketone (MEK) (30 mL), under magnetic stirring and  $\text{N}_2$  atmosphere. The reaction mixture was refluxed for 72 h, and the solvent was then distilled off; water (20.0 mL) was added to the residue, which was extracted with diethyl ether ( $4 \times 35.0$  mL). The organic layer was separated and dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by chromatography over silica gel (230–400 mesh) using ethyl acetate:hexane (5:95) as eluent, to give 1.8 g of hdacac (46% yield, mp  $39$ – $41^\circ\text{C}$ ) [26].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 0.88 (*t*, 3H,  $J = 6.8$  Hz, H-19), 1.25 (*m*, 28H, from H-5 to H-18), 1.83 (*q*, 2H,  $J = 7.4$  Hz, H-4), 2.17 (*s*, 6H, H-1), 3.61 (*t*, 1H,  $J = 7.4$  Hz, H-3).

#### 2.2.2. $\text{Eu}^{3+}$ complexes

The synthesis of  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$  was performed by mixing the corresponding sodium salt of hdacac (Nahdacac) [28] and  $\text{EuCl}_3$  (obtained by dissolution of  $\text{Eu}_2\text{O}_3$  Rhône-Poulenc/Rhodia 99.99% in concentrated hydrochloric acid) in a water/ethanol solution 1:1, pH  $\sim 6.5$

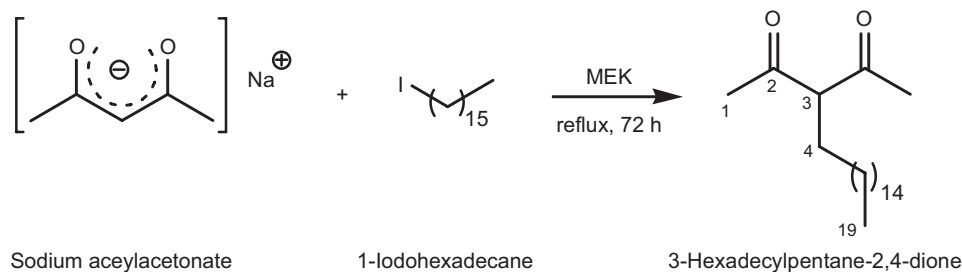


Fig. 1. Scheme of the preparation of 3-hexadecylpentane-2,4-dione.

( $\text{Eu}^{3+}:\text{hdacac} = 1:1$ ). The reaction mixture was stirred for 12 h at  $35^\circ\text{C}$ . Later, the flask was stoppered and cooled in a refrigerator overnight. After filtration, the resulting solid was washed with cool water and dried at room temperature under reduced pressure ( $\sim 50\%$  yield).

Aiming at increasing photoluminescence, the complexes  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$  and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  were synthesized. To this end, 1,10-phen (Mallinckrodt Chemical) and tta (Acros) were added at a 1:1 ratio (approximately) [8,29] to ethanolic solutions containing the compound obtained as described above.

### 2.2.3. Miscibility study

In order to evaluate the presence of  $\text{Eu}^{3+}$  ions in non-polar solvents, saturated solutions ( $\sim 1.0 \text{ mg mL}^{-1}$ ) of  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  in hexane were prepared by stirring and mild heating ( $50^\circ\text{C}$ ). After centrifugation (10 min, 2000 rpm) for elimination of non-solubilized complex, the resulting clear solutions were analyzed by luminescence spectroscopy.

### 2.2.4. Surface pressure–area isotherms and LB films

Surface pressure–surface area ( $\pi$ - $A$ ) isotherm measurements and LB film deposition were performed at  $25^\circ\text{C}$  in a Langmuir with a total area of  $296 \text{ cm}^2$  (Insight, Brazil). Surface pressure–area ( $\pi$ - $A$ ) curves were recorded at  $25^\circ\text{C}$  by spreading  $60 \mu\text{L}$  of a  $1.0 \text{ mmol L}^{-1}$   $\text{Na}(\text{hdacac})$  solution on subphases containing water or an  $\text{Eu}^{3+}$   $0.10 \text{ mmol L}^{-1}$  solution, after 15 min standing just for solvent evaporation, and after 2 h for  $\text{Eu}^{3+}$  complexation.

The LB films were formed on quartz substrates by transferring the  $\text{hdacac}$  monolayer formed on a subphase containing  $\text{Eu}^{3+}$   $0.10 \text{ mmol L}^{-1}$ . The transfer was carried out at a surface pressure of  $30 \text{ mN m}^{-1}$  and at a dipping rate of  $0.038 \text{ mm s}^{-1}$ . Z-type LB films were formed, the deposition beginning with the quartz plate immersed in the subphase solution before the spreading. Three layers of  $\text{hdacac}$  monolayer were deposited by means of a sequence of three vertical withdrawals, keeping the surface pressure constant at  $30 \text{ mN m}^{-1}$ . The SEM images together with the EDS analysis allowed verification of the  $\text{Eu}^{3+}$  distribution within the LB films. Moreover, LB-film luminescence and absorption spectra were recorded.

## 3. Results and discussion

### 3.1. Complexometric titration

The  $\text{Eu}^{3+}$  percent in  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$  complex was determined by complexometric titration with a standard edta solution, using xylenolorange as indicator. This analysis showed the following mass percents for  $\text{Eu}^{3+}$  in the complex (found/expected): 6.87/7.13.

### 3.2. Thermogravimetric analysis

TGA reveals that the total weight loss is 91.07% for the complex  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$ , as shown in Fig. 2. This led to the following mass percentages of  $\text{Eu}^{3+}$  in the complex: 7.70/7.13 (found/expected). The TGA curve has three steps of weight loss ( $157\text{--}257$ ,  $257\text{--}350$ , and  $400\text{--}490^\circ\text{C}$ ). In the two first cases, the weight losses are of 79%, and these steps are due to volatilization, decomposition of organic ligands, and loss of  $\text{H}_2\text{O}$  (adsorbed or belonging to the  $\text{Eu}^{3+}$  coordination sphere). In the third step, the weight loss (11%) is due to the decomposition of the remaining organic ligands and possible oxycarbonates formed during the analysis.

### 3.3. Elemental analysis

The analytical data of C and H percent data (found/expected) for  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$  are C: 70.8/71.0 and H: 12.0/11.4, respectively. In spite of the unsatisfactory drying due to the low thermal stability of the complexes, these results confirm the molar ratio 1:6 ( $\text{Eu}^{3+}:\text{ligand}$ ) for the complex, as well as approximately two hydration waters.

The performed volumetric and gravimetric analyses corroborate the  $\text{Eu}^{3+}:\text{ligand}$  ratio of 1:6 for the complexes, with satisfactory relative error. The presence of six ligands in each “structural unity” is a result of the hydrophobic interactions between the hydrocarbon chains. This arrangement possibly corresponds to the most stable organization of  $\text{Eu}^{3+}$  and  $\text{hdacac}$  in polar solvents, so crystallization of  $\text{hdacac}$  complexes may occur with maintenance of these interactions in the solid state. The suggested structure for this complex (Fig. 3) is possible by assuming that  $\text{Hhdacac}$  groups (i.e. protonated  $\text{hdacac}$  groups) also act as ligands for

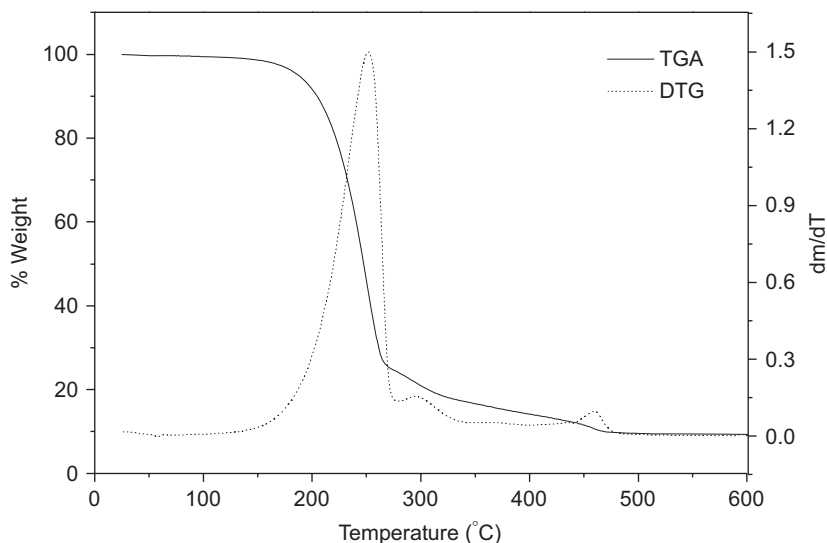


Fig. 2. TGA/DTG curves of  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$ .

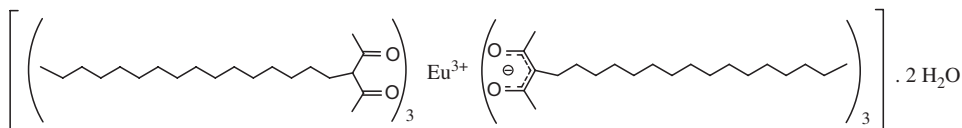


Fig. 3. Suggested structure of  $\text{Eu}(\text{hdacac})_3 \cdot (\text{Hhdacac})_3 \cdot 2\text{H}_2\text{O}$ .

$\text{Eu}^{3+}$ . The 3-hexadecyl-2,4-pentanodione and 3-hexadecyl-2,4-pentanodionate ligands contain a long aliphatic chain that confers on them a higher nucleophilicity for the carbonyl groups when compared with simple  $\beta$ -diketones. As described below, the dodecaordinated structure of  $\text{Eu}^{3+}$  is consistent with the analyses by infrared and luminescence spectroscopies.

### 3.4. Infrared spectroscopy

The FT-IR spectra (Fig. 4) exhibit two bands relative to  $\text{C}=\text{O}$  symmetric and asymmetric stretchings (at  $1724$  and  $1706\text{ cm}^{-1}$ , respectively) of the hdacac free ligand. Moreover, bands related to the enolic form are observed at  $1604\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretching) and  $3450\text{ cm}^{-1}$  (hydrogen bonded-OH groups) [30]. The  $\text{C}=\text{O}$  band is displaced to lower frequencies ( $1712\text{ cm}^{-1}$ ) in the complexes, providing a good evidence that the metal is coordinated through the oxygen atoms [31]. The characteristic bands of the ligands phen and tta are also observed in the infrared spectra. For  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$ , bands at  $1580\text{ cm}^{-1}$  (aromatic  $\text{C}=\text{C}$  stretching) and  $856\text{ cm}^{-1}$  ( $\text{C}-\text{H}$  out of ring plane) are observed. For  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$ , the band related to  $\text{C}=\text{C}$  stretching of the thenoyl group is present [30]. An intriguing aspect of the IR analysis is the superposition of all carbonyl absorption bands, either on hdacac or on Hhdacac forms. The  $\text{C}=\text{O}$  stretchings of coordinating Hdacac groups are quite similar to the stretchings of hdacac groups, as a result of the high inducting effect of the

aliphatic substituent on carbon 3 and the distortion on the charge distribution of Hhdacac ligands promoted by  $\text{Eu}^{3+}$  (a highly polarizing cation) [7,31]. So, all the 12 carbonyl groups surrounding  $\text{Eu}^{3+}$  have the same characteristics due to the polarizing action of the metallic center (and relative delocalization of the negative charges) and the electron donating character of the hexadecyl groups.

### 3.5. Luminescence spectroscopy

The excitation spectra (Fig. 5) of the prepared complexes display the characteristic excitation band of  $\text{Eu}^{3+}$  ( $^5\text{L}_6$  level) at  $393\text{ nm}$ , as well as ligand excitation broad bands below  $380\text{ nm}$ , as a result of the antenna effect. This fact arises from the delocalization of  $\pi$ -electrons in the  $\beta$ -diketones, which both stabilizes the bonds of the complex and lowers the energy of the triplet-excited state of the ligands. The substitution of hydration  $\text{H}_2\text{O}$  by phen or tta removes the non-radiative decays caused by weak couplings of the  $\text{Eu}^{3+}$  excited states with the OH oscillators, resulting in an increase in the photoluminescence intensities. As expected, this also causes an increase in the relative intensities of ligand excitations, indicating that these species are coordinated to the activator center. Moreover, the absorption spectra reveal that the excitation bands are displaced to lower energies when compared to the absorption bands of the free ligands (in hexane at room temperature); this also indicates the coordination of Hhdacac, phen, and tta with the  $\text{Eu}^{3+}$  ion. It is clearly

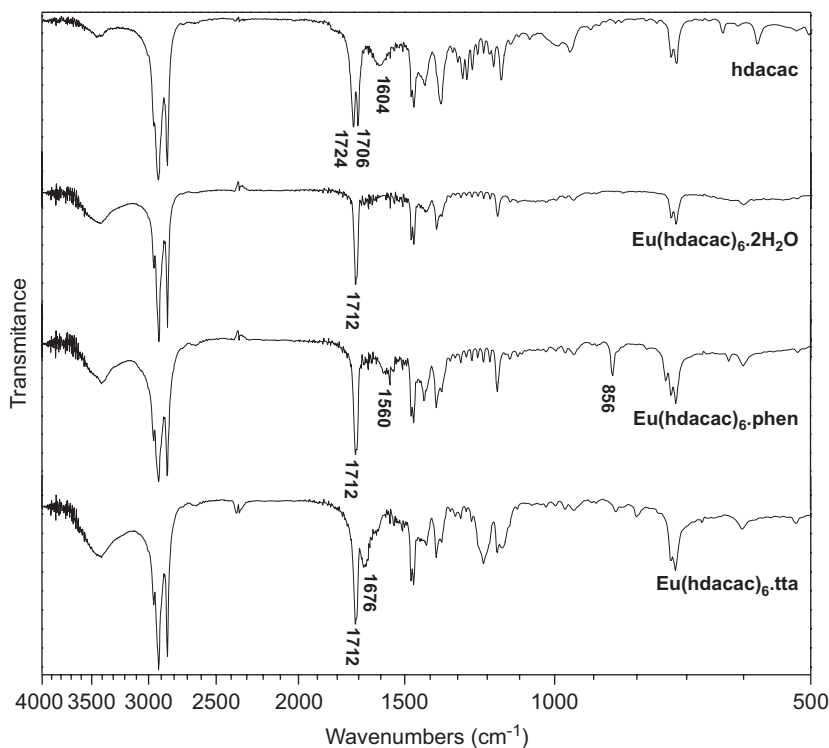


Fig. 4. Infrared spectra of Hhdacac,  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$ , and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$ , in KBr pellets.

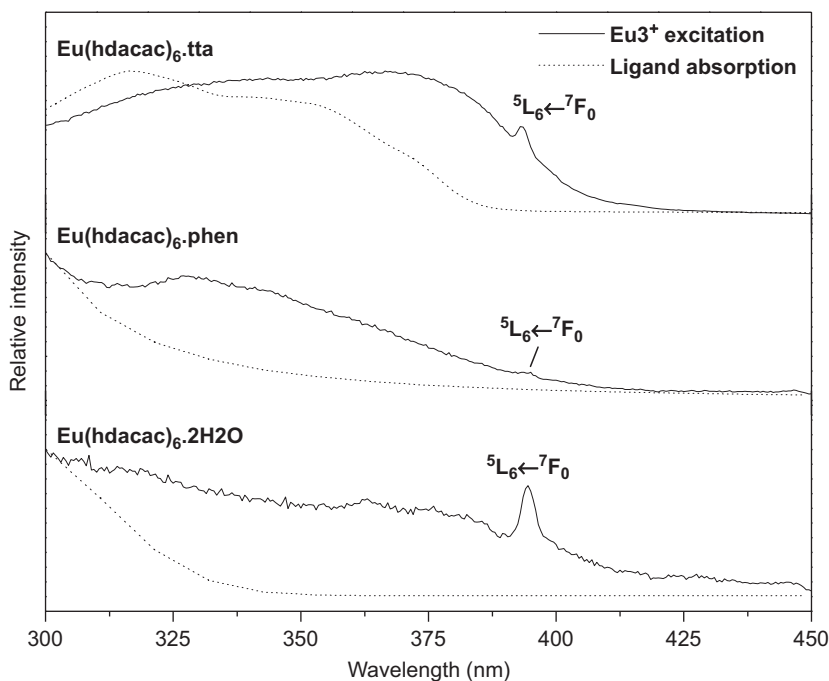


Fig. 5. Excitation spectra (solid lines) of  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}(\text{s})$ ,  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}(\text{s})$  ( $\lambda_{\text{em}} = 613 \text{ nm}$ ), and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}(\text{s})$  ( $\lambda_{\text{em}} = 611 \text{ nm}$ ), and absorption spectra (dot lines) of the free ligands in hexane.

observable that  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$  and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  are strongly excitable over all the low-energy ultraviolet region of the spectrum (UV-A).

The emission spectra of  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$ , and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  (Fig. 6) display the

characteristic  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J = 0-4$ ) transitions of  $\text{Eu}^{3+}$  under excitation at  ${}^5\text{L}_6$  level, or under ligand excitation. The three compounds show similar spectral distribution of the emission bands, indicating that the ligands indenture promotes similar chemical environment in all compounds,

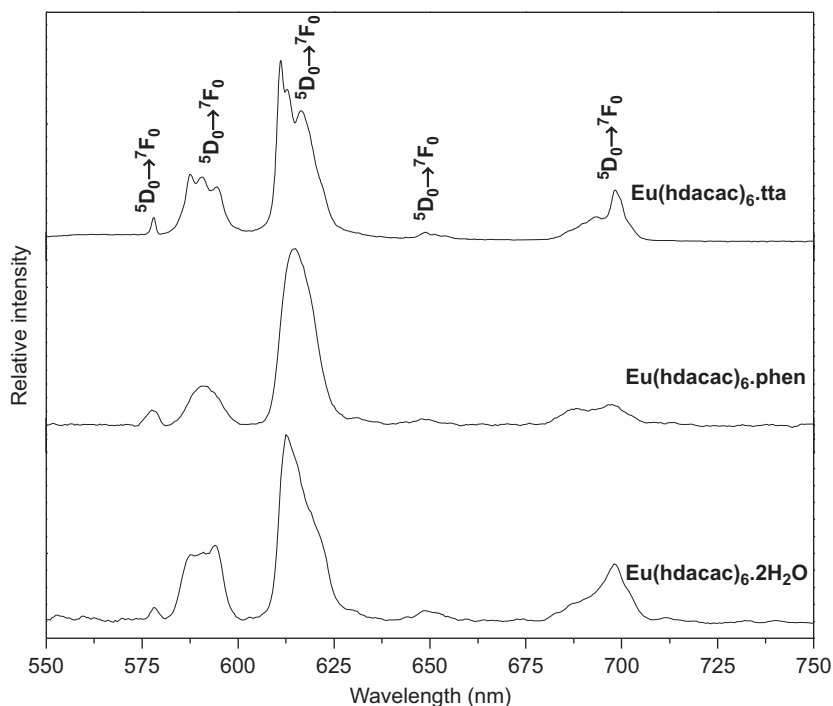


Fig. 6. Emission spectra ( $\lambda_{\text{exc}} = 330$  nm) of  $\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}(\text{s})$ ,  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}(\text{s})$ , and  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}(\text{s})$ , at room temperature.

being the difference on the efficiency of the energy transfer by the antenna effect. The highest emission intensity and the highest band definition are observed in  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$ . The hypersensitive  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition is predominant in all cases, indicating that  $\text{Eu}^{3+}$  may lie in symmetry sites without inversion center [32]. Moreover, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition is unique (though not narrow) in  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$ , showing that  $\text{Eu}^{3+}$  occupies symmetry sites with similar properties [33]. The  $\text{Eu}^{3+}$  emission profile in the complexes, with a single band in  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ , three unfoldings in  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ , and three in  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions, indicates that the activator center occupies low symmetry sites ( $\text{C}_1$ ,  $\text{C}_s$ ,  $\text{C}_2$ ,  $\text{C}_{2v}$ ) [34]. Although there are approximately 12 equivalent carbonyl groups surrounding the  $\text{Eu}^{3+}$  ion, the spatial distribution of the ligands around the metallic center (driven not only by repulsions, but also by the hydrophobic interactions) leads to the occupation of low symmetry sites. As seen from Table 1, the relations between integrated areas of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transitions also indicate that  $\text{Eu}^{3+}$  lies in a non-centrosymmetric site [32]. However, the values for the prepared complexes are relatively low when compared with those of many other  $\text{Eu}^{3+}$   $\beta$ -diketonates [7], which indicates that more symmetric environments may be occupied in the present case, as a result of the resemblance of the 12 carbonyl groups (evidenced in the FT-IR analysis). The broad emission bands, which compromises the color purities of these complexes ( $x \approx 0.60$  and  $y \approx 0.39$  [35]), are due to the non-rigid environment surrounding the  $\text{Eu}^{3+}$  ion.

The  ${}^5\text{D}_0$  level luminescence lifetimes of  $\text{Eu}^{3+}$  in the different  $\beta$ -diketonates (Table 1) were obtained at room temperature by monitoring the maximum of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$

Table 1

Luminescence lifetimes, radiative and non-radiative decay rates, excited state quantum efficiencies ( ${}^5\text{D}_0$  level), and ratios between  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  integrated areas for the prepared  $\text{Eu}^{3+}$   $\beta$ -diketonates

	$\tau_1$ (ms)	$A_{\text{RAD}}$ ( $\text{s}^{-1}$ )	$A_{\text{NRAD}}$ ( $\text{s}^{-1}$ )	$\Phi$ (%)	$I_{02}/I_{01}$
$\text{Eu}(\text{hdacac})_6 \cdot 2\text{H}_2\text{O}$	0.33	226	2787	7.5	2.3
$\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$	0.56	378	1422	21	4.9
$\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$	0.31	264	2606	9.2	2.6

transition under ligand excitation. The experimental decays were fitted by a first-order exponential decay, but they suggest the existence of several distinct coordination sites for  $\text{Eu}^{3+}$  in each system [33,36]. This also suggests that up to six ligands can coordinate  $\text{Eu}^{3+}$ : three anionic (balancing the positive charges) and the remaining neutral, besides other neutral species ( $\text{H}_2\text{O}$ , phen or tta) attached to the metal. The short values of luminescence lifetimes that are coherent with those reported on literature [7] can be explained by taking into account two factors. First, the activator centre occupies non-rigid environments, and it is surrounded by many types of vibrational oscillators that, depending on their frequency, contribute to non-radiative depopulation of the excited state [32,36]. Besides this fact, one also has to consider that  $\text{Eu}^{3+}$  is present in high concentrations, so cross-relaxation and other concentration quenching processes may be regarded [32,36]. The high value of  $\tau_1$  for  $\text{Eu}(\text{hdacac})_6 \cdot \text{phen}$  is a consequence of the structural rigidity of the bulky 1,10-phenanthroline rings, which causes a decrease of the non-radiative decays by vibrational interactions or by energy transfer between the  $\text{Eu}^{3+}$  ions.

Table 1 also shows the radiative ( $A_{\text{RAD}}$ ) and non-radiative ( $A_{\text{NRAD}}$ ) decay rates and  $^5\text{D}_0$  excited state quantum efficiencies ( $\Phi$ ), calculated from the emission spectra [37,38]. The rate of non-radiative processes is always larger than the rate of radiative decays, thus confirming that the non-radiative mechanisms of excited state depopulation are predominant. Although high emission intensities are observed (in particular for phen and tta complexes), the energy output is relatively low, once the quantum efficiencies lie between 7.5% and 21%.

### 3.6. Miscibility of $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$

The behavior of  $\text{Eu}^{3+}$  in the complex  $\text{Eu}(\text{hdacac})_6 \cdot \text{tta}$  in hexane solution was monitored by luminescence spectroscopy. Solutions containing different concentrations of this complex (from  $0.5 \text{ g L}^{-1}$  to saturation) have the same emission and excitation spectra. The presence of  $\text{Eu}^{3+}$  in the solubilized form in hexane indicates that the ligand is capable of introducing lanthanide ions (and other metals) into non-polar solutions. The dissolved complex displays a distribution of emission bands similar to the spectral distribution of the solid complex, indicating that it maintains its fundamental structure (typical of  $\text{Eu}^{3+}$   $\beta$ -diketonates) in non-polar solutions.

### 3.7. Surface pressure isotherms and LB films

The  $\pi$ - $A$  isotherms (Fig. 7) reveal that the formation of  $\text{Eu}(\text{hdacac})_n \cdot x\text{H}_2\text{O}$  at the interface depends on the contact time between hdacac and  $\text{Eu}^{3+}$  ions at the interface. Fig. 7 shows  $\pi$ - $A$  isotherms obtained in different subphases: water and  $\text{EuCl}_3$   $1.0 \times 10^{-4} \text{ mol L}^{-1}$  after 15 min of hdacac

spreading (standing for solvent evaporation), or after 120 min (for  $\text{Eu}^{3+}$  complexation). For the isotherms obtained after 15 min of spreading, we can observe the shielding effect of  $\text{Eu}^{3+}$  ions between hdacac molecules decreasing the compressibility of the isotherm only, but after 120 min the isotherms become more compressible. The expansion of the isotherms after 120 min shows that the  $\text{Eu}^{3+}$ -hdacac complexation occurs through formation of larger structures, making the packing difficult.

The monolayers obtained after 120 min of hdacac spreading were transferred to solid supports by the LB technique. Z-type LB films were formed beginning with immersion of quartz plates in the subphase solution before the spreading. Three layers of hdacac monolayers were deposited in a sequence of three vertical withdrawals while keeping the surface pressure constant at  $30 \text{ mN m}^{-1}$ . We were not successful in obtaining Y-type films. In fact, the monolayers were not transferred to the solid substrate, showing that the hydrophobic interactions between the apolar chains were not favored.

The distribution of  $\text{Eu}^{3+}$  through the LB film was verified by EDS mapping (not shown). The mappings show a reasonable distribution of  $\text{Eu}^{3+}$  on the solid substrate, attesting the LB film homogeneity. As a result of the presence of few layers in the prepared films, the UV-vis spectra of these materials do not display any significant absorption band.

The emission spectra of LB films were performed with films containing three layers of the  $\text{Eu}(\text{hdacac})_n$  complex. The films also exhibited the characteristic  $^5\text{D}_0 \rightarrow ^5\text{F}_J$  radiative transitions of  $\text{Eu}^{3+}$  under 353 nm excitation (Fig. 8). The emission profile of  $\text{Eu}^{3+}$  in the films was similar to that in the solid complexes, although a lower

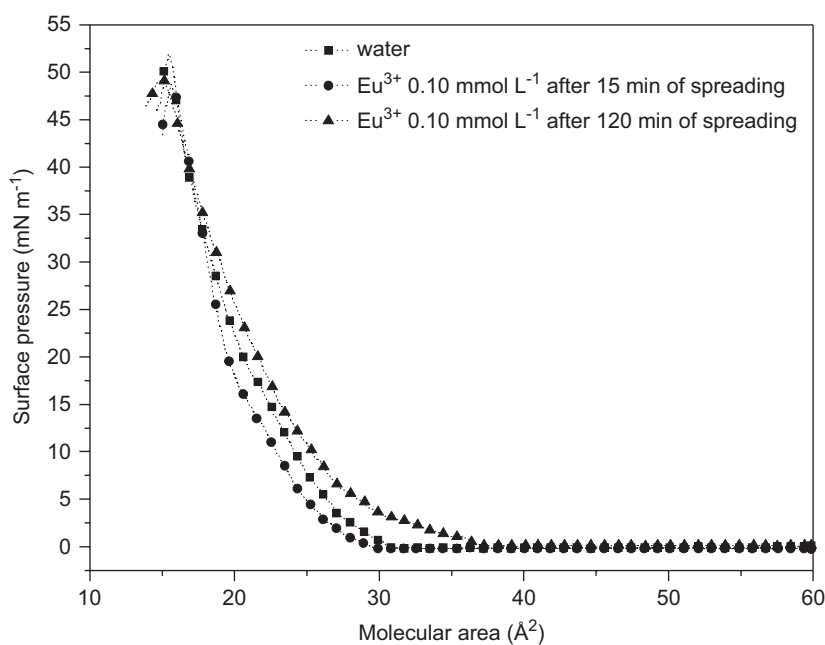


Fig. 7. Surface pressure curves of hdacac monolayers formed on water (■) or  $\text{EuCl}_3$   $0.10 \text{ mmol L}^{-1}$  subphases: after 15 min of spreading (●), and after 120 min of spreading (▲).

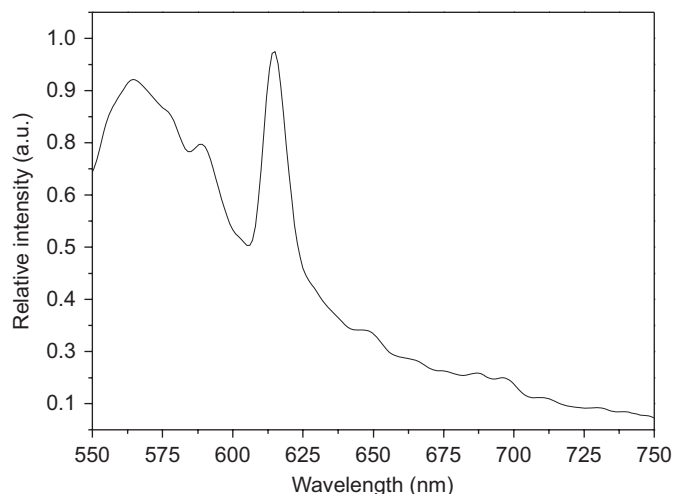


Fig. 8. Emission spectrum of three layers of the Eu(hdacac) complex in the LB film ( $\lambda_{exc} = 353$  nm).

definition of bands was observed. One should be aware that the observed signal is due to only  $< 1$  pmol of  $\text{Eu}^{3+}$  in the beam spot, estimated from the ligand molecular area. Therefore, the results attest the successful *in situ* formation of the  $\text{Eu}(\text{hdacac})_n$  complex at the Langmuir trough, with the corresponding Z-type LB films exhibiting luminescent properties, making this ligand suitable for the development of thin ordered luminescent films.

#### 4. Conclusions

A new amphiphilic ligand (Hhdacac) for rare-earth ions was synthesized. The obtained solid  $\text{Eu}^{3+}$  complexes presented a  $\text{Eu}^{3+}$ :ligand ratio of 1:6, as a result of the interactions between the neighbor aliphatic chains in the solid state. The complexes are satisfactorily miscible in hexane. Due to its amphiphilic properties, the ligand is able to introduce metallic cations into non-polar ambients, which enables the use of these complexes in probes in hydrophobic homogeneous solutions, or in metal fuel additives (Cu, Fe, or Ce) complexes, for example, the luminescent properties of the complexes were analyzed, and an increase in the photoluminescence was observed by introducing phen or tta, because of a more efficient energy transfer (antenna effect).

The characteristics of these compounds were also applied to obtain highly homogeneous luminescent Langmuir–Blodgett films, with thickness of few ( $\sim 3$ ) layers. Small differences in the photophysical properties of  $\text{Eu}^{3+}$  in the films and in the solids are observed, besides the characteristic antenna effect. Thus, hdacac can be used to obtain LB thin films of several compositions, rendering materials that can be potentially applied in photoluminescent organic–inorganic films, OLEDs, waveguides, and other devices that require a high molecular array.

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#### References

- [1] S.I. Weissman, *J. Chem. Phys.* 10 (1942) 214.
- [2] G.A. Crosby, R.E. Whan, R.M. Alire, *J. Chem. Phys.* 34 (1961) 743.
- [3] G.A. Crosby, R.E. Whan, J.J. Freeman, *J. Phys. Chem.* 66 (1962) 2493.
- [4] Y.S. Yang, M.L. Gong, Y.Y. Lei, S.L. Wu, *J. Alloys Compd.* 207/208 (1994) 112.
- [5] G.H. Morrison, H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1966, p.157.
- [6] J. Rydberg, C. Musikas, G.R. Choppin, *Practices of Solvent Extraction*, Marcel Dekker, New York, 1992.
- [7] K. Binnemans, in: K.A. Gschneidner Jr., J.-C.G. Bünzli, V.K. Pecharsky (Eds.), *Handbook on the Physics and Chemistry of the Rare Earths*, Elsevier, Amsterdam, 2005 (Chapter 225).
- [8] A.O. Ribeiro, P.S. Calefi, A.M. Pires, O.A. Serra, *J. Alloys Compd.* 374 (2004) 151.
- [9] C. Molina, K. Dahmouche, Y. Messaddeq, S.J.L. Ribeiro, M.A.P. Silva, V.Z. Bermudez, L.D. Carlos, *J. Lumin.* 104 (2003) 93.
- [10] G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. Simas, *Cood. Chem. Rev.* 196 (2006) 165.
- [11] Q. Meng, L. Fu, J. Lin, H. Zhang, S. Wang, Y. Zhou, M. Yu, F. Liu, *J. Phys. Chem. Solids* 64 (2003) 63.
- [12] S. Umetani, *J. All. Compd.* 408 (2006) 981.
- [13] D.-J. Quian, K.-Z. Yang, H. Nakahara, K. Fukuda, *Langmuir* 13 (1997) 5925.
- [14] R.-J. Zhang, K.-Z. Yang, *Langmuir* 13 (1997) 7141.
- [15] R.-J. Zhang, K.-Z. Yang, *Thin Solid Films* 178 (2001) 177.
- [16] O.A. Serra, I.L.V. Rosa, C.L. Medeiros, M.E.D. Zaniquelli, *J. Lumin.* 60–61 (1994) 112.
- [17] C.L. Medeiros, O.A. Serra, M.E.D. Zaniquelli, *Thin Solid Films* 248 (1994) 115.
- [18] R.F. Silva, M.E.D. Zaniquelli, O.A. Serra, I.L. Torriani, S.G.C. de Castro, *Thin Solid Films* 324 (1998) 245.
- [19] G.-L. Zhong, Y.-H. Wang, C.-K. Wang, B.-Y. Pu, Y. Feng, K.-Z. Yang, J.-I. Jin, *J. Lumin.* 99 (2002) 213.
- [20] D.-J. Qian, H. Nakahara, K. Fukuda, K.-Z. Yang, *Langmuir* 11 (1995) 4491.
- [21] K. Wang, L. Gao, C. Huang, *J. Photochem. Photobiol. A* 156 (2003) 39.
- [22] R. Zhang, K. Yang, *Coll. Surf. A* 178 (2001) 177.
- [23] Z. Bian, K. Wang, L. Jin, C. Huang, *Coll. Surf. A* 257–258 (2005) 67.
- [24] D. Abatti, M.E.D. Zaniquelli, Y. Iamamoto, Y.M. Idemori, *Thin Solid Films* 310 (1–2) (1997) 296.
- [25] L. Caseli, F.S. Vinhado, Y. Iamamoto, M.E.D. Zaniquelli, *Colloids Surf. A—Physicochem. Eng. Aspects* 229 (1–3) (2003) 169.
- [26] C. Cativiela, J.L. Serrano, M.M. Zurbano, *J. Org. Chem.* 60 (1995) 3074.
- [27] J.M. Kerr, C.J. Suckling, P. Bamfield, *J. Chem. Soc. Perkin Trans. 1* (1990) 887.
- [28] R.G. Charles, *Org. Synth. Coll.* 4 (1963) 869.
- [29] N. Sabbatini, M. Guardigli, *Coord. Chem. Rev.* 123 (1993) 201.
- [30] D. Pavia, G. Lampman, G. Kriz, *Introduction to Spectroscopy*, Third ed., Thomson Learning, Toronto, 2001 (Chapter 2).
- [31] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fourth ed., Wiley, New York, 1986 (Part I and Part III).



- [32] G. Blasse, B.C. Grammaier, *Luminescent Materials*, Springer, Berlin, 1994 (Chapter 3).
- [33] P. Porcher, in: R. Saez, P.A. Caro (Eds.), *Rare Earths*, Editorial Complutense, Madrid, 1999 (Chapter 3).
- [34] J.H. Forsberg, *Coordin. Chem. Rev.* 10 (1973) 195.
- [35] P.A. Santa-Cruz, F.S. Teles, *Spectra Lux Software v.2.0*, Ponto Quântico Nanodispositivos/RENAMI, 2003.
- [36] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), *Lanthanide Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam, 1989 (Chapter 7).
- [37] C. de Mello Donegá, S. Alves Júnior, G.F. de Sá, *J. Alloys Compd.* 250 (1997) 422.
- [38] C.A. Kodaira, H.F. Brito, O.L. Malta, O.A. Serra, *J. Lumin.* 101 (2001) 11.