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

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Abstract

This work reports on the synthesis and characterization of the ligand 3-hexadecylpentane-2,4-dione (Hhdacac) and its Eu$^{3+}$ complexes Eu(hdacac)$_6\cdot$2H$_2$O, Eu(hdacac)$_6\cdot$phen and Eu(hdacac)$_6\cdot$tta, where phen and tta denote 1,10-phenanthroline and thenoyltrifluoroacetone, respectively. These new compounds present long carbon chains and their expected miscibility into non-polar ambient is confirmed by the emission spectra of Eu(hdacac)$_6\cdot$tta in hexane. Moreover, the amphiphilic properties of Eu(hdacac)$_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 (1H 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, \(\beta\)-diketones (1,3-diketones) give rise to very attractive absorption bands not to mention their many other particular properties. The \(\beta\)-diketones are known for being able to qubate 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 has 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 Eu$^{3+}$, Sm$^{3+}$, and 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,
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 [17,18]. LB films of this type may be otherwise forced to exchange some subphase containing the ion of interest [17,18]. LB films with a lipid that spreads easily in an aqueous hydrophobic subambient, which enables its spreading at the air/liquid interface [16]. This peculiar substitution on the carbon between the two carbonyl groups, which allows a better distribution of the chelating agent around the ion. The structure of the synthesized ligand was confirmed by 1H nuclear magnetic resonance (1H NMR). The compositions of the prepared Eu3+ complexes were elucidated by complexometric titration (Eu3+/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 ambient, as shown by the emission spectra of Eu(hdacac)6·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 ambient, as precursors for organic–inorganic photo- or electro-luminescent devices, and for LB films with many attractive characteristics.

2. Experimental

2.1. Apparatus

1H NMR spectra were acquired on a Bruker AVANCE 400 spectrometer. Measurements were carried out at room temperature (∼300 K). Deuterated chloroform (CDCl3) 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 °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 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 (∼300 K), using a SPEX Triax 550 Fluorolog III spectrophotometer. 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 N2 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 × 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 Eu(hdacac)6·2H2O (from now on we denote Eu(hdacac)6·2H2O, assuming x ≈ 2). Eu(hdacac)3, phen, and Eu(hdacac)6·ttta (phen = 1,10-phenanthroline, tta = thenoyltrifluoroacetone). This peculiar β-diketone contains a substituent on the carbon between the two carbonyl groups, which allows a better distribution of this chelating agent around the ion.

Due to their long aliphatic chains (amphiphilic character), the synthesized complexes are miscible in hydrophobic ambient, as shown by the emission spectra of Eu(hdacac)6·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 ambient, as precursors for organic–inorganic photo- or electro-luminescent devices, and for LB films with many attractive characteristics.
(Eu$^{3+}$:hdacac = 1:1). The reaction mixture was stirred for 12 h at 35°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 (~50% yield).

Aiming at increasing photoluminescence, the complexes Eu(hdacac)$_6$/C$_1$phen and Eu(hdacac)$_6$/C$_1$ttta were synthesized. To this end, 1,10-phen (Mallinckrodt Chemical) and tta (Acros) were added at a 1:1 ratio (approximately) to ethanolic solutions containing the compound obtained as described above.

2.2.3. Miscibility study

In order to evaluate the presence of Eu$^{3+}$ ions in non-polar solvents, saturated solutions (~1.0 mg mL$^{-1}$) of Eu(hdacac)$_6$·ttta in hexane were prepared by stirring and mild heating (50°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°C in a Langmuir with a total area of 296 cm$^2$ (Insight, Brazil). Surface pressure–area ($\pi$–$A$) curves were recorded at 25°C by spreading 60 µL of a 1.0 mmol L$^{-1}$ Nahdacac solution on subphases containing water or an Eu$^{3+}$ 0.10 mmol L$^{-1}$ solution, after 15 min standing just for solvent evaporation, and after 2 h for Eu$^{3+}$ complexation.

The LB films were formed on quartz substrates by transferring the hdacac monolayer formed on a subphase containing Eu$^{3+}$ 0.10 mmol L$^{-1}$. The transfer was carried out at a surface pressure of 30 mN m$^{-1}$ and at a dipping rate of 0.038 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 hdacac monolayer were deposited by means of a sequence of three vertical withdrawals, keeping the surface pressure constant at 30 mN m$^{-1}$. The SEM images together with the EDS analysis allowed verification of the 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 Eu$^{3+}$ percent in Eu(hdacac)$_6$·2H$_2$O, complex was determined by complexometric titration with a standard edta solution, using xyleneflorange as indicator. This analysis showed the following mass percents for 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 Eu(hdacac)$_6$·2H$_2$O, as shown in Fig. 2. This led to the following mass percentages of Eu$^{3+}$ in the complex: 7.70/7.13 (found/expected). The TGA curve has three steps of weight loss (157–257, 257–350, and 400–490°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 H$_2$O (adsorbed or belonging to the 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 Eu(hdacac)$_6$·2H$_2$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 (Eu$^{3+}$:ligand) for the complex, as well as approximately two hydration waters. The performed volumetric and gravimetric analyses corroborate the Eu$^{3+}$: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 Eu$^{3+}$ and hdacac in polar solvents, so crystallization of 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 Hdacac groups (i.e. protonated hdacac groups) also act as ligands for
The FT–IR spectra (Fig. 4) exhibit two bands relative to C=O symmetric and asymmetric stretchings (at 1724 and 1706 cm\(^{-1}\), respectively) of the hdacac free ligand. Moreover, bands related to the enolic form are observed at 1604 cm\(^{-1}\) (C=C stretching) and 3450 cm\(^{-1}\) (hydrogen bonded–OH groups) [30]. The C=O band is displaced to lower frequencies (1712 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 Eu(hdacac)\(_6\)+phen, bands at 1580 cm\(^{-1}\) (aromatic C=C stretching) and 856 cm\(^{-1}\) (C–H out of ring plane) are observed. For Eu(hdacac)\(_6\)+ tta, the band related to C=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 C=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 Eu\(^{3+}\) (a highly polarizing cation) [7,31]. So, all the 12 carbonyl groups surrounding 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 Eu\(^{3+}\) (\(^5\)\(L_6\) level) at 393 nm, as well as ligand excitation broad bands below 380 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 H\(_2\)O by phen or tta removes the non-radiative decays caused by weak couplings of the 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 Eu\(^{3+}\) ion. It is clearly
observable that Eu(hdacac)$_6$phen and Eu(hdacac)$_6$tta are strongly excitable over all the low-energy ultraviolet region of the spectrum (UV-A).

The emission spectra of Eu(hdacac)$_6$·2H$_2$O, Eu(hdacac)$_6$phen, and Eu(hdacac)$_6$tta (Fig. 6) display the characteristic $^5$D$_0$→$^7$F$_J$ ($J = 0$–$4$) transitions of Eu$^{3+}$ under excitation at $^5$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,
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 Eu(hdacac)6·tta. The hypersensitive $^5D_0 \rightarrow ^7F_2$ transition is predominant in all cases, indicating that Eu$^{3+}$ may lie in symmetry sites without inversion center [32]. Moreover, the $^5D_0 \rightarrow ^7F_0$ transition is unique (though not narrow) in Eu(hdacac)6·tta, showing that Eu$^{3+}$ occupies symmetry sites with similar properties [33]. The Eu$^{3+}$ emission profile in the complexes, with a single band in $^5D_0 \rightarrow ^7F_0$, three unfoldings in $^5D_0 \rightarrow ^7F_1$, and three in $^5D_0 \rightarrow ^7F_2$ transitions, indicates that the activator center occupies low symmetry sites (C1, C2, C2v) [34]. Although there are approximately 12 equivalent carbonyl groups surrounding the 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 $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions also indicate that 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 Eu$^{3+}$ β-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 Eu$^{3+}$ ion.

The $^7F_0$ level luminescence lifetimes of Eu$^{3+}$ in the different β-diketonates (Table 1) were obtained at room temperature by monitoring the maximum of the $^5D_0 \rightarrow ^7F_2$ 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 Eu$^{3+}$ in each system [33,36]. This also suggests that up to six ligands can coordinate Eu$^{3+}$: three anionic (balancing the positive charges) and the remaining neutral, besides other neutral species (H$_2$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 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 Eu(hdacac)6·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 Eu$^{3+}$ ions.

<table>
<thead>
<tr>
<th>Eu(hdacac)6·2H$_2$O</th>
<th>Eu(hdacac)6·phen</th>
<th>Eu(hdacac)6·ttta</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (ms)</td>
<td>$A_{RAD}$ (s$^{-1}$)</td>
<td>$A_{NRAD}$ (s$^{-1}$)</td>
</tr>
<tr>
<td>0.33</td>
<td>226</td>
<td>2787</td>
</tr>
<tr>
<td>0.56</td>
<td>378</td>
<td>1422</td>
</tr>
<tr>
<td>0.31</td>
<td>264</td>
<td>2606</td>
</tr>
</tbody>
</table>

Table 1: Luminescence lifetimes, radiative and non-radiative decay rates, excited state quantum efficiencies ($^5D_0$ level), and ratios between $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ integrated areas for the prepared Eu$^{3+}$ β-diketonates.
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 Eu(hdacac)$_6$·tta

The behavior of Eu$^{3+}$ in the complex Eu(hdacac)$_6$·tta in hexane solution was monitored by luminescence spectroscopy. Solutions containing different concentrations of this complex (from 0.5 g L$^{-1}$ to saturation) have the same emission and excitation spectra. The presence of 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 Eu$^{3+}$-diketonates) in non-polar solutions.

3.7. Surface pressure isotherms and LB films

The $\pi$–$A$ isotherms (Fig. 7) reveal that the formation of Eu(hdacac)$_n$·$x$H$_2$O at the interface depends on the contact time between hdacac and Eu$^{3+}$ ions at the interface. Fig. 7 shows $\pi$–$A$ isotherms obtained in different subphases: water and EuCl$_3$ 1.0 x $10^{-4}$ mol L$^{-1}$ after 15 min of hdacac spreading (standing for solvent evaporation), or after 120 min (for Eu$^{3+}$ complexation). For the isotherms obtained after 15 min of spreading, we can observe the shielding effect of 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 Eu$^{1+}$–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 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 Eu$^{3+}$ through the LB film was verified by EDS mapping (not shown). The mappings show a reasonable distribution of 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 Eu(hdacac)$_n$ complex. The films also exhibited the characteristic $^5\text{D}_0$→$^5\text{F}_J$ radiative transitions of Eu$^{3+}$ under 353 nm excitation (Fig. 8). The emission profile of 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 EuCl$_3$ 0.10 mmol L$^{-1}$ subphases: after 15 min of spreading ( ), and after 120 min of spreading (▲).](image-url)
differences in the photophysical properties of Eu3+ in the Blodgett films, with thickness of few (to obtain highly homogeneous luminescent Langmuir–transfer (antenna effect).

introducing phen or tta, because of a more efficient energy and an increase in the photoluminescence was observed by additives (Cu, Fe, or Ce) complexes, for example, the hydrophobic homogeneous solutions, or in metal fuel which enables the use of these complexes in probes in to introduce metallic cations into non-polar ambients, hexane. Due to its amphiphilic properties, the ligand is able solid state. The complexes are satisfactorily miscible in interactions between the neighbor aliphatic chains in the solid.

The obtained solid Eu3+ complexes presented a Eu3+: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 ambient, 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 (~3) layers. Small differences in the photophysical properties of Eu3+ 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.

4. Conclusions

A new amphiphilic ligand (Hhdacac) for rare-earth ions was synthesized. The obtained solid Eu3+ complexes presented a Eu3+: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 ambient, 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).

Fig. 8. Emission spectrum of three layers of the Eu(hdacac) complex in the LB film (λexc = 353 nm).

definition of bands was observed. One should be aware that the observed signal is due to only <1 pmol of Eu3+ in the beam spot, estimated from the ligand molecular area.

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