



## Formation of thin luminescent $\text{Eu}^{3+}$ -LB films by *in situ* coordination with 2,3,5,6-tetra(2'-pyridyl)pyrazine and 1-octadecanol in pure and mixed Langmuir monolayers

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### ABSTRACT

The *in situ* complexation between 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) molecules and europium ions at the air–liquid interface by means of mixed 1-octadecanol Langmuir films is reported. These films were transferred to solid supports by means of the Langmuir–Blodgett (LB) technique. The EDS maps attested the homogeneity of the LB films as well as the presence of the europium ions. The mixed alcohol/tppz LB film contained a larger amount of europium ions as compared to the pure octadecanol LB film. This work reports the production of a thin luminescent  $\text{Eu}^{3+}$  film containing europium ions using only alcohol molecules as ligands—an unexpected result, since it is well known that there is an occurrence of non-radiative deactivation of excited europium by hydroxyl groups. Europium ion multiple binding sites were detected from lifetime decay measurements of these films in the presence of tppz molecules.

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### 1. Introduction

Complexes formed between metals and nitrogen heterocyclic ligands play an important role in the supramolecular chemistry field [1,2]. The large interest in this kind of molecules stems from their notable magnetic and conducting properties [3–5]. Moreover, the use of polynuclear complexes formed between metals and aromatic nitrogen heterocycles as bridging ligands has long been attractive for the study of photoinduced electron and energy transfer [6,7]. Thin films containing rare earth complexes have been employed in electroluminescent devices due to their particular spectroscopic features like the presence of narrow bands in the luminescence spectra with the possibility of energy transfer [8]. On the other hand, polypyridine-type ligands are particularly interesting because they form very stable complexes with a wide range of transition metals in multiple oxidation states [9,10]. One of these ligands is the multi-ring heterocycle 2,3,5,6-tetra(2'-pyridyl)pyrazine (tppz), which was first reported by Goodwin and Lions [11]. Fig. 1 shows the chemical structure of tppz.

The synthesis and characterization of complexes formed between transition metals and tppz have been reported [12–16]. In fact, steric difficulties have been noted in earlier reports, but it

has been demonstrated that tppz can act as a bis(tridentate) bridging ligand between identical or different metal centers, resulting in fascinating electronic and magnetic materials. Works on complexes formed between tppz and with rare earth ions are still lacking [17–19], but the stepwise formation of a complex between tppz and a series of metal ions ( $\text{M}^{n+}$ ) including some rare earths has been described in acetonitrile solution [17], and it has been demonstrated that tppz forms a 2:1 complex [(tppz)<sub>2</sub>- $\text{M}^{n+}$ ] and a 1:1 complex [tppz- $\text{M}^{n+}$ ] with  $\text{M}^{n+}$  at low and high concentrations of metal ions, respectively. Quasi-stoichiometric 2:1 [(tppz)<sub>2</sub>- $\text{M}^{n+}$ ] complexes have been detected in the case of trivalent metal ions as well as in the case of the divalent metal ions  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , and it has been shown that they act as strong Lewis acids. The intensity of tppz fluorescence becomes noticeable at high concentrations of metal ions, because the 2:1 (tppz)<sub>2</sub>- $\text{M}^{n+}$  species are converted into the fluorescent 1:1 tppz- $\text{M}^{n+}$  complex. These systems are regarded as an “OFF–OFF–ON” fluorescence sensor for metal ions depending on the stepwise formation of the tppz–metal ion complex.

Initial experiments carried out by our group have attempted the isolation of tppz–lanthanide complexes from solution, but tppz segregation occurred in all cases. This has prompted us to use the Langmuir monolayers for production of tppz–lanthanide complexes *in situ* at the air/water interface, which should enable their subsequent transfer to solid supports by means of the LB technique. In fact, the reactivity of small amounts of metal ions with monolayer forming compounds is not new. Perhaps the first

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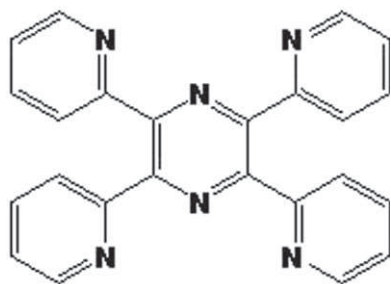


Fig. 1. Structure of the ligand 2,3,5,6-tetra(2'-pyridyl)pyrazine (tppz).

report on this issue was authored by Mitchell et al. in the 30's [20]. Recently, *in situ* chemical reaction at the Langmuir trough has been used to produce nanowires consisting of platinum-plated DNA molecules [21]. The incorporation of rare earth ions into LB films comprised of relatively simple amphiphilic molecules has also been reported [22–28]. These films have been successfully transferred to solid supports by means of the LB technique, which provides ultrathin films of the rare earth complexes with molecular arrangement, as detected by X-ray diffraction [25]. Strong luminescence has been recorded for different ligands, and signal could be detected even for a single layer of ligands such as dihexadecyl phosphate [23],  $\beta$ -diketonate [24], and p-dodecanoyloxybenzoate [27]. Gomes et al. [29] have observed that the formation of  $\text{Eu}(\text{hdacac})_n \cdot x\text{H}_2\text{O}$  (hdacac: 3-hexadecylpentane-2,4-dionate) depends on the contact time between hdacac and europium ions at the interface. In this case, the hdacac monolayers were transferred to solid supports by means of the LB technique, and Z-type LB films were obtained; the emission profile of  $\text{Eu}^{3+}$  in these films was similar to the one observed for the solid complexes. The results thus attested to the successful *in situ* formation of the  $\text{Eu}(\text{hdacac})_n$  complex at the Langmuir trough, making this ligand suitable for the development of thin, ordered luminescent films.

Therefore, the apparent impossibility of isolating the europium–tppz complex from solution and the numerous successful cases of *in situ* formation of rare earth complexes and their transfer by the LB technique have motivated us to study this system. In this work, evidence that  $\text{Eu}^{3+}$  coordinates with tppz as well as with a fatty alcohol is presented on the basis of surface pressure curves, luminescence spectra, scanning electron microscopy, and energy-dispersive X-ray (EDS) analysis. The complexes were prepared using mixed Langmuir monolayers of 1-octadecanol and tppz. Although deactivation of the  $\text{Eu}^{3+}$  radiative emission by the OH oscillator is well known, the luminescence spectra recorded for octadecanol– $\text{Eu}^{3+}$  LB films were typical of that observed for  $\text{Eu}^{3+}$ .

## 2. Experimental details

### 2.1. Reactants and solutions

1-Octadecanol (99%) was purchased from Sigma-Aldrich. The  $\text{EuCl}_3$  aqueous solution was prepared from the respective oxide (99.99%, Aldrich) by dissolution in hydrochloric acid, which was followed by careful evaporation of the excess acid, and further dilution in dust-free deionized water (resistivity  $\sim 18 \text{ M}\Omega \text{ cm}$ ). The obtained solution was employed in the preparation of a  $0.1 \text{ mol L}^{-1}$  stock solution and further diluted. The tppz ligand (Fig. 1) was synthesized according to the Goodwin and Lions method [11]. All the  $1 \text{ mmol L}^{-1}$  1-octadecanol and tppz solutions were prepared in chloroform (J.T. Baker-HPLC Grade).

### 2.2. Formation of Langmuir monolayers and LB films

Surface pressure–surface area ( $\pi$ -A) measurements were conducted at  $25 \pm 1 \text{ }^\circ\text{C}$  in a  $216 \text{ cm}^2$  Langmuir trough (Insight, Brazil), by spreading a  $1.0 \text{ mmol L}^{-1}$  pure octadecanol solution or a  $1.0 \text{ mmol L}^{-1}$  octadecanol/tppz 1:2 mixture dissolved in chloroform on an aqueous  $0.1 \text{ mmol L}^{-1}$   $\text{Eu}^{3+}$  subphase (pH 5.0). The barrier was compressed at  $0.42 \text{ mm s}^{-1}$  after 30 min of monolayer spreading, in order to guarantee solvent evaporation and tppz complexation with  $\text{Eu}^{3+}$ . The LB films were formed by transferring the monolayers to Si (1 0 0) or quartz supports at  $30 \text{ m N m}^{-1}$  constant surface pressure. The transfer was carried out at a dipping rate of  $0.038 \text{ mm s}^{-1}$ .

### 2.3. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDS) analysis

The SEM images and the EDS maps of the LB films were acquired on a Zeiss (mod. EVO 50) scanning electron microscope and an IXRF system (mod. 500 Digital Processing) spectrometer, respectively.

### 2.4. Luminescence studies

The emission and excitation spectra were recorded at room temperature on a Horiba Jobin-Yvon Spex Triax 550 Fluorolog 3 spectrofluorometer equipped with a 450-W continuous xenon lamp. The detection was performed with a Hamamatsu R928P photomultiplier. Filters were placed in the excitation and emission beams, in order to improve the quality of the acquired spectra. For the emission spectra, the entrance and exit slits were adjusted, so as to obtain resolutions of 10–12 and 2 nm, respectively, for the excitation spectra, the resolutions were 2 and 10 nm. All the films were positioned in the sample chamber at an angle of  $22.5^\circ$  relative to the detector, so as to minimize scattering and reflection effects. Luminescence lifetime measurements were carried out using a SPEX 1934D phosphorimeter and a 150-W pulsed xenon lamp.

## 3. Results and discussion

### 3.1. Mixed octadecanol:tppz Langmuir monolayers

The interaction between amphiphilic molecules and luminescent complexes on Langmuir monolayers has been widely studied [30,31]. However, just a few research groups have explored the *in situ* formation of luminescent complexes at Langmuir monolayers. In this work, the *in situ* complexation between tppz and  $\text{Eu}^{3+}$  at the air/liquid interface has been investigated. Since tppz itself does not form a monolayer at the air/liquid interface, a non-ionic amphiphilic compound with a high spreading coefficient was selected and mixed with tppz. The fatty alcohol 1-octadecanol was the compound of choice because of its well documented surface pressure isotherm, in spite of the expected non-radiative deactivation of the europium luminescence by the hydroxyl groups.

The pure octadecanol monolayer exhibits the typical  $\pi$ -A curve (Fig. 2) with minimum area at  $21 \pm 1 \text{ \AA}^2$ , in accordance with the previous results of Ref. [32]. In Fig. 2 it can also be observed that 1-octadecanol monolayers are affected by the presence of tppz and  $\text{Eu}^{3+}$ . Both tppz and  $\text{Eu}^{3+}$  cause expansion of the monolayers, confirming that the tppz molecules are adsorbed at the air/liquid interface even though this ligand is not amphiphilic. On the basis of these results, it is possible to

state that  $\text{Eu}^{3+}$  can interact with both alcohol and tppz molecules present at the air/liquid interface.

Table 1 summarizes the particular features of the isotherms. In the presence of  $\text{Eu}^{3+}$  in the subphase, both pure octadecanol and mixed octadecanol/tppz monolayers have minimum molecular areas that are larger than those found for the same monolayers when they are formed on water as subphase. This increase in the minimum area can be related to the complexation of  $\text{Eu}^{3+}$  with the alcohol molecules as well as with the tppz molecules present at the interface. Higher values of minimum molecular area in the presence of  $\text{Eu}^{3+}$  had already been observed for monolayers containing charged amphiphilic molecules such as carboxylic acids [23].

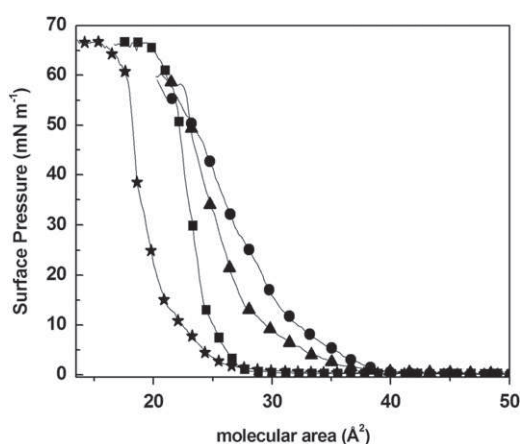


Fig. 2.  $\pi$ -A isotherms for monolayers of pure 1-octadecanol on water (\*), on  $0.1 \text{ mmol L}^{-1} \text{Eu}^{3+}(\text{aq})$  subphase (■) and octadecanol/tppz 2:1 mixture on water (▲), and on  $0.1 \text{ mmol L}^{-1} \text{Eu}^{3+}(\text{aq})$  subphase (●).

Table 1

Minimum molecular area of pure and mixed octadecanol LB monolayers, intensity ratios between the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transitions, and  $\text{Eu}^{3+}$  luminescence lifetimes ( ${}^3\text{D}_0$ ) for the obtained samples.

Sample	Subphase	Minimum molecular area ( $\text{\AA}^2$ )	$I_{02}/I_{01}$	$\tau$ (ms)
<b>LB films</b>				
Octadecanol	Water	20.9	–	–
Octadecanol	$\text{EuCl}_3(\text{aq})$	24.9	4.2	$0.45 \pm 0.05$
1 Tppz: 2 octadecanol	$\text{EuCl}_3(\text{aq})$	33.0	5.4	$0.29 \pm 0.03$
1 Tppz: 2 octadecanol	Water	28.2	–	–
<b>Bulk samples</b>				
Octadecanol- $\text{Eu}^{3+}$	–	–	1.9	–
$\text{EuCl}_3$	–	–	0.97	–

### 3.2. 1-Octadecanol and 1-octadecanol-tppz LB films: SEM-EDX characterization

Langmuir monolayers of pure octadecanol and mixed octadecanol/tppz formed on  $0.1 \text{ mmol L}^{-1} \text{Eu}^{3+}$  solutions were successfully transferred to silicon slices and coated with carbon, in order to obtain SEM images and EDS maps. The goal of the SEM-EDS studies was to determine the distribution of the alcohol and tppz molecules as well as of  $\text{Eu}^{3+}$  in the LB films, as judged from the oxygen, nitrogen, and  $\text{Eu}^{3+}$  signals (Fig. 3A–D). The EDS map of the Si (100) slice without the LB film is shown in Fig. 4 for comparison purposes.

Oxygen and nitrogen atoms were detected throughout the whole mixed LB film, which reveals a homogeneous distribution of the alcohol and tppz molecules, respectively, without segregation. The oxygen atoms content in the Si (100) slice (Fig. 4A) is not significant as compared to the oxygen atoms content in the LB film (Fig. 3A).  $\text{Eu}^{3+}$  ions (Fig. 3C and D) are present in the film as islands; i.e., their distribution is heterogeneous in both the films containing alcohol only and in the films consisting of alcohol and tppz. Thus, it is likely that not all the alcohol and tppz molecules are complexed with  $\text{Eu}^{3+}$ . However, it is evident that the amount of  $\text{Eu}^{3+}$  transferred to the films containing tppz is higher than that present in the pure octadecanol films. Therefore,  $\text{Eu}^{3+}$  complexation should occur through the OH groups of the alcohol and the nitrogen atoms of the tppz molecules. In order to corroborate this finding, the films were also analyzed by luminescence spectroscopy.

### 3.3. Luminescence studies

In order to record the emission spectra, Langmuir monolayers were transferred to quartz plates. Fig. 5 displays the emission and excitation spectra of pure 1-octadecanol and mixed 1-octadecanol/tppz LB films obtained from the aqueous  $\text{EuCl}_3$  subphase.

The  $\text{Eu}^{3+}$  ions are effectively transferred to the LB films, as evidenced by the emission bands at 590 and 614 nm, which correspond to the characteristic  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  electronic transitions of  $\text{Eu}^{3+}$ , respectively. The first transition is magnetic dipole-allowed, and thus its intensity (as well as its radiative decay rate) is practically independent of the chemical environment in which the  $\text{Eu}^{3+}$  ion is placed. On the other hand, the second transition occurs through forced electric dipole and vibronic coupling mechanisms, thus being hypersensitive to the symmetry around  $\text{Eu}^{3+}$  and also being affected by the ligand polarizability. In the absence of an inversion center, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition is intensified due to the relaxation of the Laporte rule [33,34]. In the emission spectra of the prepared LB films, the first observation is that the presence of tppz molecules (in a 1:2 ratio with regard to 1-octadecanol) reduces the overall emission intensity of the spectrum. For example, the band at 614 nm is almost three times more intense in the 1-octadecanol-LB film as compared to the same band in the case of the mixed

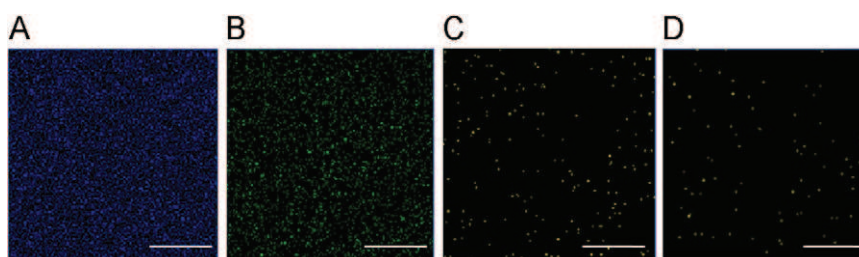


Fig. 3. EDS elemental distribution pattern of the prepared LB films: (a) oxygen, (b) nitrogen, (c)  $\text{Eu}^{3+}$  in mixed alcohol/tppz LB films, and (d)  $\text{Eu}^{3+}$  in alcohol LB films. The scale bar corresponds to 100  $\mu\text{m}$ .

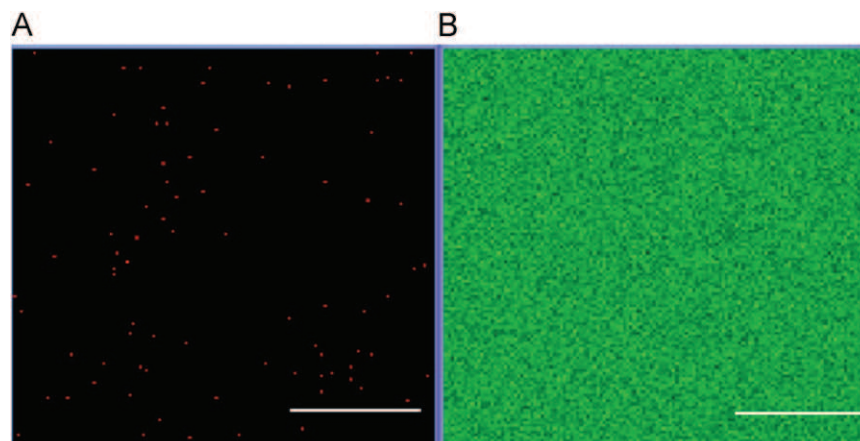


Fig. 4. EDS elemental distribution pattern of the native Si (1 0 0) slice: (a) oxygen and (b) silicon. The scale bar corresponds to 100  $\mu\text{m}$ .

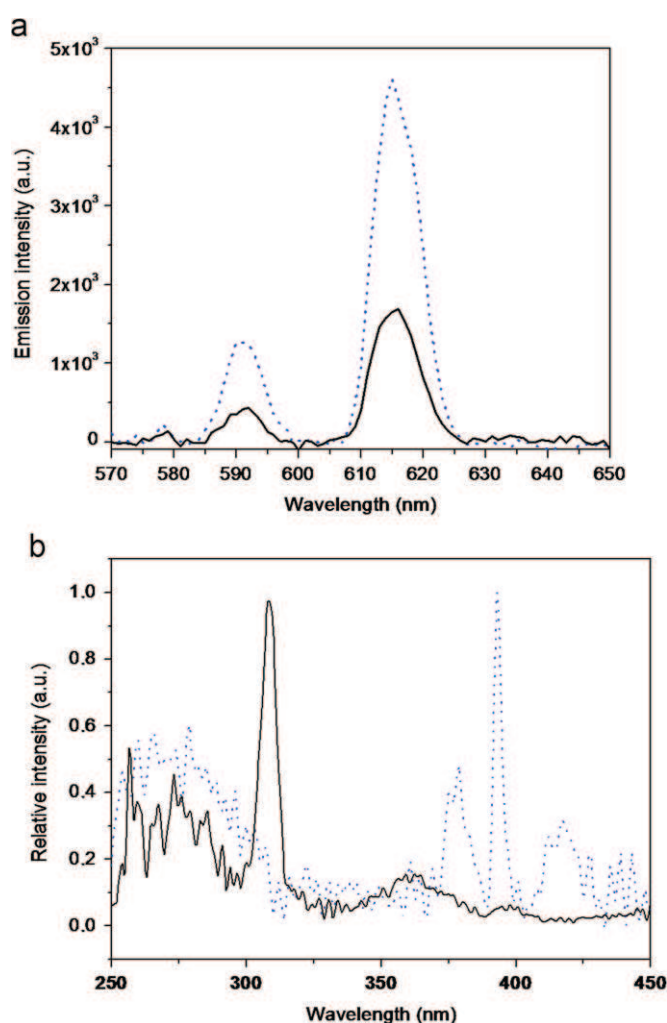


Fig. 5. (a) Emission and (b) normalized excitation spectra of the LB films transferred from the  $\text{Eu}^{3+}_{(aq)}$  subphase: 1-octadecanol (blue dotted lines,  $\lambda_{em}=614$  nm,  $\lambda_{exc}=394$  nm); 1-octadecanol/tppz (black solid lines,  $\lambda_{em}=614$  nm,  $\lambda_{exc}=310$  nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

1-octadecanol/tppz-LB film. In other words, the emission intensity can be related to the presence of the tppz ligand in the films, which seems to be responsible for the quenching of the  $\text{Eu}^{3+}$  luminescence. Besides, attention should be paid to the differences

in the minimum areas for both isotherms (Table 1), which means that different surface densities can be obtained for the films. In this way, in order to compare the chemical environment occupied by the  $\text{Eu}^{3+}$  ions in the prepared films, the ratios between the integrated intensities of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transitions ( $I_{02}/I_{01}$ , Table 1) have been recorded.

The  $I_{02}/I_{01}$  ratio is related to the symmetry of the sites occupied by the  $\text{Eu}^{3+}$  ions; the higher the centrosymmetric character of the occupied site, the lower the  $I_{02}/I_{01}$  ratio, due to the lower intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition in such conditions. In this sense, an increase of about 30% is observed for this ratio (from 4.2 to 5.4) when tppz is present at the interface, which indicates that different and less symmetric  $\text{Eu}^{3+}$  environments occur as compared to the situation where  $\text{Eu}^{3+}$  forms complexes with alcohol molecules only. This can be related to the presence of tppz and alcohol molecules acting as ligands for  $\text{Eu}^{3+}$  in the mixed films, which results in a less symmetrical coordination environment in this case. These differences are in agreement with the  $\text{Eu}^{3+}$  excitation profiles of the prepared films (Fig. 5). For the films containing only 1-octadecanol, the excitation spectrum displays the characteristic  $\text{Eu}^{3+}$  f-f absorptions in the UV range, mainly the  $^5\text{L}_6 \leftarrow ^7\text{F}_0$  absorption at 394 nm, since the alcohol molecules have a very weak energy transfer ability. On the other hand, the excitation spectrum of the mixed 1-octadecanol/tppz films displays excitation bands centered around 310 nm and 360 nm, without the occurrence of the intraconfigurational f-f absorptions. These bands attest to the coordination of the tppz groups with the  $\text{Eu}^{3+}$  ions. In this sense, an antenna effect is observed in the  $\text{Eu}^{3+}$ /tppz system at the LB film interface, with the occurrence of a ligand–metal energy transfer process.

Nevertheless, in spite of the occurrence of an antenna effect from the tppz ligand, as already mentioned, the LB films prepared in the presence of this compound have an emission intensity, which is lower than the emission of the films containing 1-octadecanol only. At a first glance, this observation could be explained by the coordination of  $\text{Eu}^{3+}$  ions to quenching species, such as water molecules or OH groups from 1-octadecanol. The reduction in the emission intensity would also occur if the tppz ligand itself acted as a quencher of the  $\text{Eu}^{3+}$  luminescence, for instance, in the case of a triplet state with lower energy than the emitting state of the lanthanide ion, as observed porphyrins and other aromatic ligands. However, both of these explanations are improbable, since the excitation spectrum of the mixed 1-octadecanol/tppz film evidences that there is an energy transfer process from tppz to  $\text{Eu}^{3+}$ , and not the opposite. Moreover, the coordination of  $\text{Eu}^{3+}$  to a higher amount of OH groups in the mixed films is unlikely because, as evidenced by the SEM–EDS maps, the presence of tppz

results in a higher  $\text{Eu}^{3+}$  surface density as compared to the films prepared with 1-octadecanol only. This demonstrates a higher affinity of the  $\text{Eu}^{3+}$  ions for the tppz ligand. Therefore, the reduction in the emission intensity can be explained by the occurrence of cross-relaxation and concentration quenching processes in the presence of tppz to a larger extent, as compared to the complex formed in the presence of 1-octadecanol only. The tppz ligand can act as a bridge between two metal centers, thus shortening the separation between the emitting ions drastically. This results in an increase in the rate of energy transfer between the identical emitting species, thereby leading to an overall decrease in the emission intensity due to the concentration quenching [31].

The luminescence lifetimes ( $^5\text{D}_0$  state) of the  $\text{Eu}^{3+}$  ions in the prepared films were also recorded by monitoring of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition (Table 1), in order to confirm the former propositions. The results attest that the attenuation of the emission intensity in the presence of tppz is accompanied by a diminution of the luminescence lifetime. The lifetime observed for the 1-octadecanol LB films was  $0.45 \pm 0.05$  ms, whereas in the presence of tppz this value was  $0.29 \pm 0.03$  ms. These data are higher than those observed when  $\text{Eu}^{3+}$  ions are coordinated to OH groups in aqueous solutions (0.12 ms [34]), thus supporting the hypothesis that the  $\text{Eu}^{3+}$  ions are not coordinated to water molecules only, but also with alcohol or alcohol/tppz molecules.

In order to compare the obtained LB films with non-ordered samples, the emission spectra of bulk samples containing 1-octadecanol (melting point 56–59 °C) and  $\text{Eu}^{3+}$  as well as samples containing the solid  $\text{EuCl}_3 \cdot x\text{H}_2\text{O}$  only (crystallized from an aqueous  $\text{EuCl}_3$  solution through evaporation) were also recorded (Fig. 6), aiming at verifying the effect of the molecular order of the LB films on the  $\text{Eu}^{3+}$  emission.

The samples were prepared by mixing about 0.08  $\mu\text{mol}$   $\text{EuCl}_3$  and 8  $\mu\text{mol}$  of melted 1-octadecanol or by drying 0.08  $\mu\text{mol}$  of an  $\text{EuCl}_3$  solution. The pellets were prepared with these samples at ambient temperature. The first difference that can be observed is the very low intensity of the  $\text{EuCl}_3$  sample emission as compared to the other samples, which is a result of the vibrational deactivation of the  $^5\text{D}_0$  level by the OH groups of water. Moreover, the measured  $I_{02}/I_{01}$  ratio for this sample is lower than unity ( $I_{02}/I_{01}=0.97$ ), thus corroborating the occurrence of sites with very high centrosymmetric character, probably due to the

presence of 6–8 water ligands in this case. On the other hand, the 1-octadecanol/ $\text{Eu}^{3+}$  pellet exhibits a spectrum with a significantly modified  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  band profile as compared to the spectra of the corresponding LB film and of the  $\text{EuCl}_3$  sample. The  $I_{02}/I_{01}$  ratio of the 1-octadecanol/ $\text{Eu}^{3+}$  pellet is also different from and lower ( $I_{02}/I_{01}=1.9$ ) than the ones achieved for the LB films, thus indicating the occurrence of sites with a higher centrosymmetric aspect. These observations lead to the conclusion that the interactions between the  $\text{Eu}^{3+}$  ions and the ligands are different in the bulk samples and that in the LB interface, and in the obtained LB films there is an effective complexation of the lanthanide ions with the 1-octadecanol and the tppz molecules. It can therefore be confirmed that the  $\text{Eu}^{3+}$  ions are effectively transferred from the monolayers to the solid supports through the polar head of the alcohol molecules, and the arrangements around  $\text{Eu}^{3+}$  in the LB films differ from those in the bulk pellets.

#### 4. Conclusion

The *in situ* complexation of tppz molecules with  $\text{Eu}^{3+}$  was successfully accomplished through formation of mixed 1-octadecanol/tppz Langmuir films at the air/liquid interface. The presence of tppz in the monolayers and of  $\text{Eu}^{3+}$  in the subphase affected the 1-octadecanol  $\pi$ -A curve, revealing that the non-amphiphilic tppz molecules can interact with alcohol molecules at the interface and with the  $\text{Eu}^{3+}$  ions present in the subphase. These films were transferred to solid supports by means of the LB technique. EDS maps and the luminescence spectra attested to the presence of  $\text{Eu}^{3+}$  ions in the LB films containing alcohol molecules only as well as in the mixed alcohol/tppz LB films. Moreover, in spite of the occurrence of non-radiative decay processes, the differences in the  $\text{Eu}^{3+}$  luminescence spectra and lifetime decay in the LB films containing alcohol and alcohol/tppz evidenced that the  $\text{Eu}^{3+}$  ions are coordinated to different binding sites in the presence of tppz, thus confirming effective interaction with this ligand.

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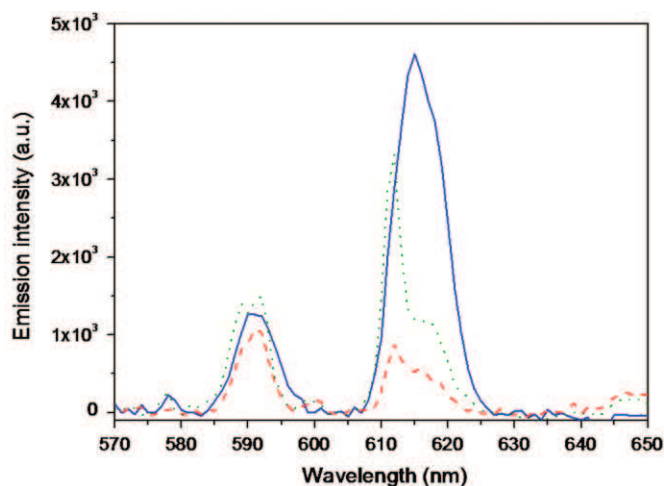


Fig. 6. Comparison between the emission spectra ( $\lambda_{\text{exc}}=394$  nm) of 1-octadecanol/ $\text{Eu}^{3+}$  LB films (blue solid line), hydrated  $\text{EuCl}_3(\text{s})$  sample (red dashed line), and 1-octadecanol/ $\text{Eu}^{3+}$  pellet (green dotted line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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