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Langmuir–Blodgett films incorporating an ionic europium complex

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ABSTRACT

Langmuir–Blodgett (LB) technique is a powerful tool to fabricate ultrathin films with highly ordered structures and controllable molecular array for efficient energy and electron transfer, allowing the construction of devices at molecular level. One method to obtain LB films consists in the mixture of classical film-forming molecules, for example Stearic Acid (SA) and functional metal complex. In this work $NH_4[Eu(bmdm)_4]$, where the organic ligand *bmdm* is (butyl methoxy-dibenzoyl-methane) or (1-(4-methoxyphenyl)-3-(4-tert-butylphenyl)propane-1,3-dione) was used to build up Langmuir and LB films. Langmuir isotherms were obtained from (i) $NH_4[Eu(bmdm)_4]$ complex and (ii) $NH_4[Eu(bmdm)_4]$/SA (1:1). Results indicated that (i) form multilayer structure; however the surface pressure was insufficient to obtain LB films, and (ii) can easily reproduce and build LB films. The dependence of number of layers in the UV absorption spectra suggest that the complex did not hydrolyze or show decomposition, UV spectral differences observed between the solution and the LB film indicate that the complex has a highly ordered arrangement in the film and the complex has an interaction with SA. Excitation spectra confirm a ligand-europium energy transfer mechanism. The transition lines of Eu^{3+} ion were observed in emission spectra of all films, the photoluminescence spectra indicate a fluorescence enhanced effect with the number of LB layers.

1. Introduction

More and more attention has been paid to rare-earth β-diketone complex Langmuir–Blodgett (LB) films in recent years for their significance both in theoretical and practical areas [1]. In particular LB films based on strong luminescence have attracted interest with respect to the correlation of film-formation and fluorescence behaviors of Eu(III) complexes with molecular and film structures, and the fabrication of advanced optoelectronic devices [2].

Three classes of amphiphilic Eu(III) complexes have been reported for LB films; (i) many workers have employed metal salts in the aqueous subphase to incorporate groups into LB films that are absorbed onto the fatty acid film from the subphase by a stochastic process [3,4]; (ii) chemical modification is used to obtain amphiphilic functional molecules to build up LB films [5,6] and (iii) the mixture of classical film-forming molecules (for example: Stearic Acid or Arachidic Acid) and functional metal complexes can be used to obtain LB films [7,8].

Effects of synergetic ligands of the europium complexes $Eu(tta)_3nL$ were tta denotes α-thenoyltrifluoroacetone and L denotes the synergetic ligands triphenylphosphine oxide (tppo), 1,10-phenanthroline (phen), 2,2′-bipy (bipy) and H_2O were studied by Wu et al. Experiments on the Langmuir trough showed that different supermolecular structures were formed for each complex with different synergetic ligands. By using Arachidic Acid (AA) good miscibility with this complex, controllable nanometer-scale thickness and vertical uniformity which allow it to be used as high quality ultrathin optical devices was observed [9]. The fabrication of $Eu(dpm)_3$ (dpm) =2,2,6,6-tetramethyl-3,5-heptanedionate mixed LB films coexisting with (AA) with different molar percentages can be deposited successfully and enhanced luminescence was observed [10].

Previously, other groups studied the ternary complex $Eu(tta)_3$phen and presented it as an efficient luminophor, however it is difficult to form organized molecular films [6]. In order to demonstrate the conditions required to fabricate good quality thin films, its surface behavior on various subphases has been exhaustively studied [5,6]. With distinct influences on the monolayer behaviors, the components of the subphase are very important to the fabrication of good quality of Langmuir and LB films; organized molecular films of $Eu(tta)_3$phen/AA (1:1) and $Sm(tta)_3$phen/AA (1:1) were then transferred onto solid substrates using the LB technique and investigated, results indicate that the two LB films can emit strong fluorescence, and that all the LB films are vertically uniform [6].

Zhang and co-workers mentioned that some problems arising from very loose packing of the europium complex in the film, and poor film-forming properties remain to be solved [11]. Although

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the addition of auxiliary film-forming materials such as Stearic Acid (SA) could improve film-forming property of the materials, this had potential phase separation difficulties and had a negative effect on fluorescent characteristics. Also, interestingly, complexes without a long alkyl chain may be used in electronic devices because of the presence of alkyl layers in LB films usually have poor vertical conduction [12].

A tetrakis complex, using a 4:1 ligand-to-metal ratio, where a single positively charged counter ion is needed to assure the electrical neutrality of the complex can be used to obtain LB films. In our previous work the synthesis and characterization of NH$_4$[Eu(bmdm)$_4$] was described [13]. Melby et al. [14] described tetrakis diketonates as potassium and sodium salts. Another example that illustrates the use of an ionic complex is europium dibenzoylmethane (hdbm), which shows that the base used should be of sufficient strength to allow an adequate ionization of the diketone for tetrakis formation [15].

Following these strategies, in the present paper, LB film made of NH$_4$[Eu(bmdm)$_4$] coexisting with stearic acid was investigated and its optical properties are reported.

2. Experimental

2.1. Materials

NH$_4$[Eu(bmdm)$_4$] complex was synthesized and purified according to Ref. [13], the purity and structure of the complex was confirmed by elemental analyses and spectroscopic characterizations. The molecular structure *bmdm* ligand (1-(4-methoxyphenyl)-3-(4-tert-butylphenyl)propane-1,3-dione) was shown in Fig. 1. Stearic Acid and chloroform were of reagent grade and used without purification.

2.2. Procedures and apparatus

Surface pressure-area π-A isotherms and LB films were obtained by means of KSV 3000. A Milli-Q system was used to produce pure water with an average resistivity of 18.2 MΩ·cm. The monolayers were formed by spreading a volume of complex solution in chloroform on the liquid surface. The solvent was allowed to evaporate 15 min prior compressing, then π-A isotherms (surface pressure versus area per molecule) were recorded. Hydrophilic glass substrates were used for fabricating LB films by the vertical deposition method in Y-type. The experiments were performed under the surface pressure of 15 mN m^{-1} at a speed of 10 mm·min^{-1} and at room temperature (25 ± 1 °C).

The UV–vis absorption spectra of LB films were collected on a PerkinElmer UV–vis Lambda 14P instrument with a blank plate as reference. The photoluminescence spectra were obtained on a FLUOROLOG SPEX 212L with a 450 W xenon continuous lamp equipped with a Hammamatsu R928 photomultiplier.

3. Results and discussion

3.1. Monolayer behaviors and LB film fabrication

Fig. 2 shows the Surface pressure–area π-A isotherm of NH$_4$[Eu(bmdm)$_4$] on the aqueous subphase, a minimum area per molecule for the liquid condensed to solid phase transition is around 20 Å^2 molecule^{-1}; the presence of charged species NH$_4$$^+$ contributed to arrangement of Langmuir film, however, the transfer from the monolayers to the solid substrates is not satisfactory.

Thus an appropriate amount of Stearic Acid (SA) was also separated mixed with complex solution to improve their transfer properties. Monolayers of NH$_4$[Eu(bmdm)$_4$]/SA (1:1) are stable and easy to transfer onto solid substrates; on the other hand, unstable mixed monolayers were obtained by using concentration higher than the equimolecular one, as observed at π-A isotherm of the NH$_4$[Eu(bmdm)$_4$]/SA (1:2). The π-A isotherm of the mixed monolayer was shown in Fig. 3, liquid-condensed (LC) and liquid-expanded (LE) phases were assigned. A limiting molecular area was derived to be 80 Å^2 molecule^{-1} in the condensed solid region of isotherm by extrapolation to zero value of area per molecule. The result indicated that β-diketonate complexes molecule must form multilayer condensed structure at high surface pressure at air–water interface due to the poor amphiphilic properties of rare earth β-diketonate complex. It also indicated that SA molecules should remain in monolayer structure in the mixed film.

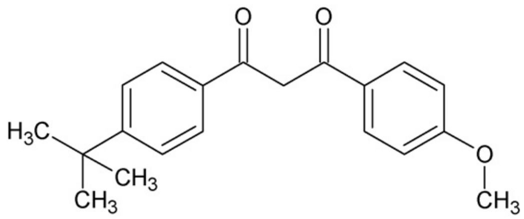

Fig. 1. Molecular structure of the *bmdm* (1-(4-methoxyphenyl)-3-(4-tert-butylphenyl)propane-1,3-dione) ligand.

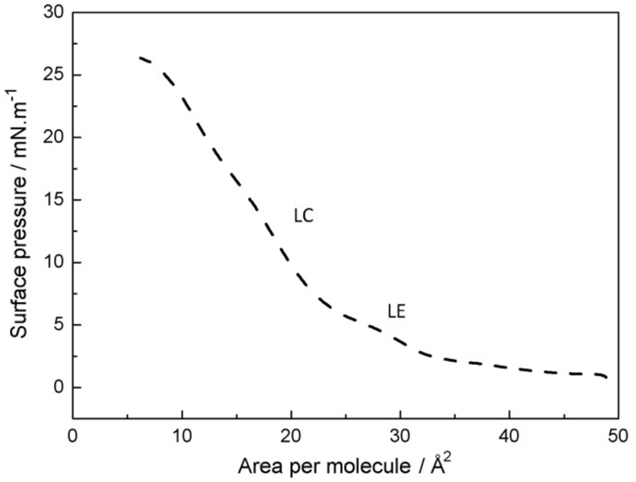

Fig. 2. Surface pressure–area isotherm for NH$_4$[Eu(bmdm)$_4$] on the aqueous subphase.

UV–vis spectroscopy of NH$_4$[Eu(bmdm)$_4$]/SA (1:1) LB films in different number of layers was shown in Fig. 4. The wavelength of the absorption peaks of LB films kept unchanged, while the intensities of the absorption peaks increased. The inset Fig. 4 shows a plotter absorbance at 294 nm against number of layers deposited, the linear dependence of the absorbance on the number of layers can be obtained for 11, 21 and 31 layers LB films; considering that the intensity of absorption is determined by the amount of the complex a deviation from linearity was observed just for one

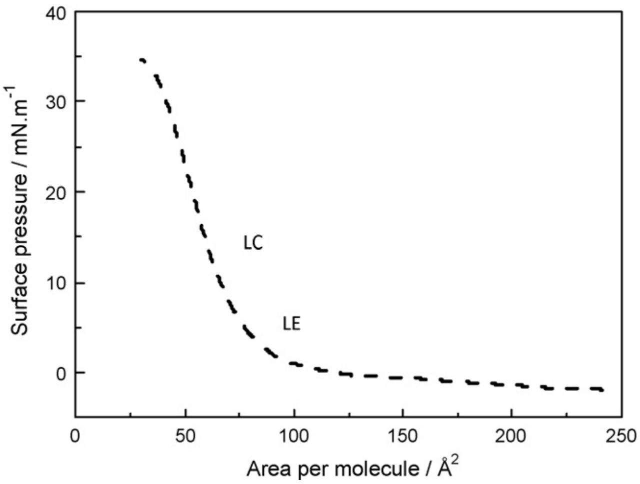

Fig. 3. Surface pressure–area isotherm for NH$_4$[Eu(bmdm)$_4$]/SA (1:1) monolayer on the aqueous subphase.

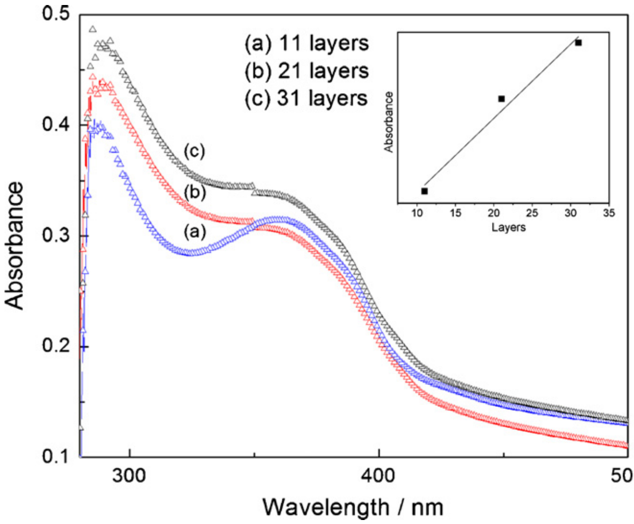

Fig. 4. UV–vis spectra of $NH_4[Eu(bmdm)_4]$/SA (1:1) LB film in different number of layers: (a) 11 layers, (b) 21 layers and (c) 31 layers. The inset is the plot of the absorbance at 294 nm versus the number of layers.

layer LB deposited, it could be explained by the sensitivity of UV–vis measurements [16,17].

Fig. 5 shows ultraviolet absorption spectra of *bmdm* ligand, $NH_4[Eu(bmdm)_4]$ and LB film. A wide UV absorption band is observed with λ_{max} = 358 nm assigned to π–π* transitions of β-diketone in both free ligand and complex spectra. In the free ligand spectrum we also observe another two bands at 265 nm and 287 nm assigned to π–π* transitions of the benzene ring and keto-enol tautomerism respectively. In the complex spectrum the band at 287 nm disappears, which is likely due to vibronic component. The LB film exhibited maximum absorption peaks at 294 nm and 363 nm which are red-shifted compared with the complex. The UV spectral differences observed between the solution and the LB film indicate that the complex has a highly ordered arrangement in the film and the complex has an interaction with SA [18].

Fig. 6 shows the excitation spectrum of a 21 and 31 layer LB films on glass substrate. It gives two bands at 254 nm and 318 nm, assigned to the ligand centered π–π* transition of the bmdm ligand. The lanthanide complex and LB films absorb energy by the *bmdm* ligand, the absorption process of lanthanide usually depends on the anion ligand, besides this the efficiency of a lanthanide complex is very sensitive to the triplet state energy as well as singlet state energy of the anion ligand; triplet state energy of ligand controls

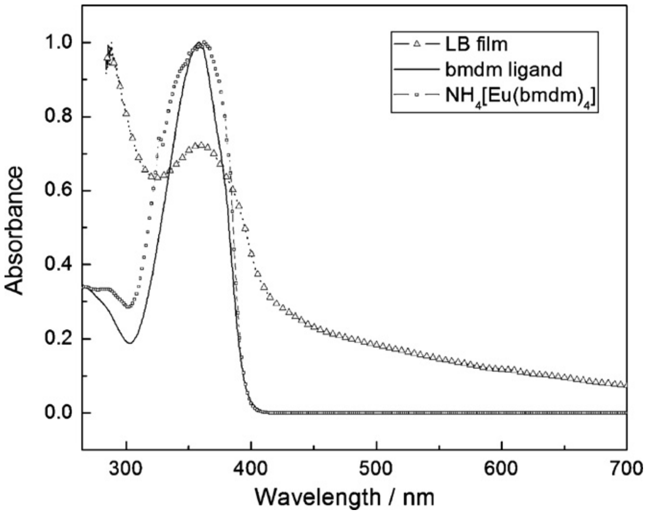

Fig. 5. UV–vis spectra of 11 layers of LB film of $NH_4[Eu(bmdm)_4]$/SA (1:1), (bmdm) ligand and $NH_4[Eu(bmdm)_4]$ complex in ethanol solution.

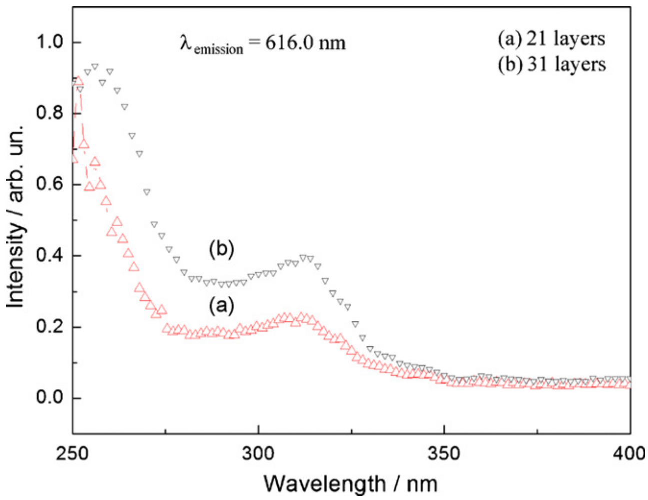

Fig. 6. Excitation spectra of $NH_4[Eu(bmdm)_4]$/SA (1:1) LB films in different number of layers: (a) 21 layers and (b) 31 layers.

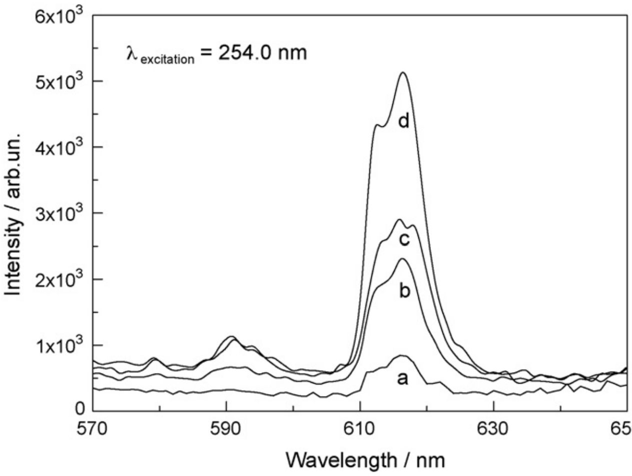

Fig. 7. Emission spectra of $NH_4[Eu(bmdm)_4]$/SA (1:1) LB films in different number of layers: (a) 1 layer, (b) 11 layers, (c) 21 layers and (d) 31 layers.

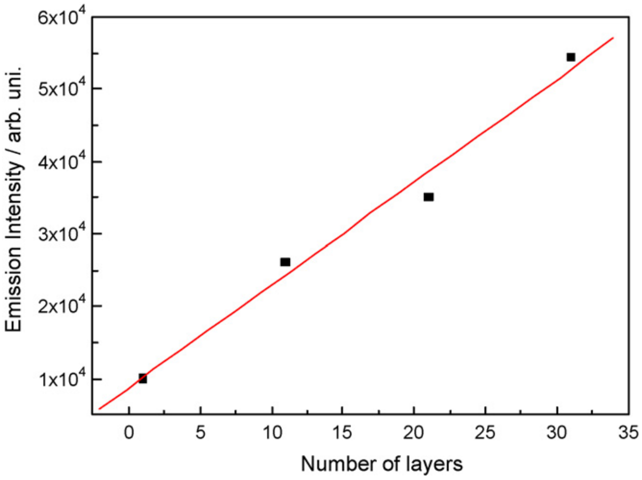

Fig. 8. Dependence of the emission intensities on the number of deposited layers.

the energy transfer between the *bmdm* ligand and central metal ion.

Fig. 7 shows the emission spectrum of LB films, it gives three characteristic peaks at 579 nm, 591 nm and 614 nm and assignable to $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1 and 2). A linearity dependence on the emission intensities versus number of layers deposited was observed in Fig. 8; this result indicates that the film transfers were reproducible and uniform, the correlation factor calculated was 0.9957.

4. Conclusions

In this work, we reported the fabrication of the mixed LB films of $NH_4[Eu(bmdm)_4]$ coexisting with stearic acid. Preliminary studies of surface pressure-area isotherm and optical properties on the Langmuir–Blodgett films of $NH_4[Eu(bmdm)_4]$/SA (1:1) showed that the complex has a good Langmuir and Langmuir–Blodgett films formation properties. UV–vis absorption band in the film was red-shifted in comparison with that in methanol solution, suggesting orientation of the transferred molecules. Y-type LB films can be deposited successfully. The luminescence intensity indicates that the film transfers were reproducible and uniform.

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