Luminescent Properties of Europium Complexes with Different Long Chains in Langmuir-Blodgett (LB) Films

Tiesheng Li¹,², Wei Shang³, Fuli Zhang¹,², Luyuan Mao³, Caiqin Tang¹,², Maoping Song¹, Chenxia Du¹,², Yangjie Wu¹,²

¹Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, The Key and Open Lab of Applied Chemistry of Henan Universities, Kaifeng, China
²Key Lab of Advanced Information Nano-Materials of Zhengzhou, Zhengzhou University, Zhengzhou, China
³Institute of Materials and Engineering, Zhengzhou University, Zhengzhou, China
E-mail: lts34@zzu.edu.cn
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Abstract

A series of europium(III) complexes with different chain length, tris [2-m-pyridylmethanamido-5-phenyl-(1,3,4)-oxadiazole] mono [2-(4-n-alkylphenyl)-iminazole (4,5-f)-1,10-phenanthroline] Eu(III) [Eu(PMA)₃Nₙ (n = 6, 10, 14, 18)] were synthesized. All of these amphiphilic europium(III) complexes could form stable Langmuir film at air/water interface and could be transferred onto hydrophilic quartz and mica substrates by measurement of UV spectra in which the absorbance of the LB films at about 288 nm scales showed the linearity with the number of layers deposited. In order to investigate relation between fluorescence properties and the arrangement of molecular in LB films, surface topography of monolayer films were observed by atomic force microscopy (AFM). Results showed that the emission spectra have Eu(III) characteristic peaks and strong emission strength. It is interesting that the molecular with looser arrangement in LB films has better monochromaticity, which illustrated that energy might transferred more easily from ligand to Eu(III) in loosen structure films.

Keywords: Europium Complex, LB Films, Photo-Luminescence, AFM

1. Introduction

The luminescent behaviors of lanthanide complexes have been widely studied due to their sharp line and long life emission, which are caused by an inter- and/or intra-molecular energy transfer from the ligands to the metal ions followed by luminescence emission [1,2]. Eu(III) complexes can give strong characteristic luminescence with long lifetime and excellent monochromaticity, so they were regarded as one of the best luminescence materials and were widely used in chemistry, physics, biochemistry and agriculture, optical amplification and waveguide, laser materials [3]. OLED [4,5], Luminescent Chemical Sensors [6]. The luminescent lanthanide complexes can be embedded in sol-gel glasses, LB films, and polymer film with the latter matrix being the preferred one [7]. Much attention has recently been attracted to the assembling of the lanthanide complexes by physical and chemical methods. Some ways based on Langmuir Blodgett (LB) films have been used to deposit many lanthanide complexes as ordered and ultrathin films. LB technique has been recognized as one of the most powerful tools of making thin films with highly ordered structure [8], which can be used to investigate the interaction and orientation among molecules in films, as well as molecular assembly and making device. Since LB technique was introduced to fabricate Eu(III) complexes films [9], many researches have been done to study their luminescence of other materials with Eu(III) complexes composition [10]. As hydrophilic ability of Eu(III) complexes was strong and were hard to form stable film on subphase, ways were done to overcome Eu(III) complexes LB films stability and weak emission strength in films [6-9,11-13]. Mixture system containing complexes and classical film-forming molecules (SA or AA) could form stable Langmuir film at air/water surface and could be fabricated excellent LB films, but film-forming molecules affected emission strength because they were hard to be controlled exact molecular packing in films [14,15]. To solve this problem, some researchers tried to utilize...
mixed subphase and got better emission spectra, but this method was complexity and the cost was expensive [16]. Thin films of lanthanide-containing polyoxometalates have been prepared by several methods, including via LB technique, [17-19]. Meanwhile, C. H. Huang et al. investigated amphiphilic Eu(III) complexes LB films without film former also showing characteristic Eu(III) emission strength [20]. Mitsuishi, M studied the LB films consisted of a mixture of poly (N-dodecyla-crylamide) and [Eu(tta)(phen)] sandwiched between poly (N-decylcrylamide) layers which were used as optical temperature sensor [21]. Qian et al., studied the monolayer assemblies of some samarium, europium, and terbium complexes with the ą-diketonate ligand thienyltrifluoroacetone and concluded that the closely packed structures of the complexes have some influences on the emissions of the lanthanoid ions, especially for the europium and samarium complexes [22,15]. However, the relationship between the emission strength and the orientation topography were not deeply studied in the researches done above. It is known that the structure and orientation of europium complexes in film can strongly affect their fluorescence properties of europium complexes. Herein, Novel amphiphilic Eu(III) complexes with symmetrical ligand and coligands with different long alkyl chain were synthesized and their LB films were fabricated without other film former in order to investigate the inference of different chains on their relationship between surface topography in films and fluorescence properties.

2. Experimental

In our design of Eu complex, we mainly consider that the type and number of ligands in the complex and the properties of filming. That is to say, one is the ligands that not classical diketone, but asymmetry one having indole group which can co-ordinated with Eu ion and one coligand which have excellent film forming properties through modifying with alkyl chain because of it being easily substituted by alkyl chains. Since the alkyl chains create a hydrophobic microenvironment, which protects the Eu$^{3+}$ ion from hydroxyl groups and the alkyl chains is easier to prepare without cracks [23,24]. Moreover, the long alkyl chain stabilizes the amorphous phase. It is known that crystallization of the emissive layer has an unfavorable effect on the electro-Luminescence [25], which resulted in an effective intermolecular energy transfer and a high sensitization efficiency [26]. Eu(PMA)$_3$N$_n$ (n = 18, 14, 10, 6) were synthesized according to the literature procedure [27-30]. Their structures were shown in Figure 1.

Synthesis of 2-(4-octadecylalk-oxyphenyl)-iminazole (4,5-f)-1, 10-Phenanthroline (N$_{18}$) 1,10-phenanthroline-5,6 diketone, 0741 oz and 3.0 g NH$_4$OAC were dispersed into 30 ml glacial acetic aci d, and heated, then 2.34 g 4-octadecyalkoxyphenyl aldehyde dropped into 10 ml glacial acetic acid and circumfluenced for 3 hours. Cooling to the room temperature and washed by 200 ml water, neutralized by aqueous ammonia to pH = 7 ~ 8, yellow sediment was filtrated, washed by water and re-crystallized in chloroform/ethanol (1:5), vacuum dried and yellow solid 3.1 g was got, yield 77%. 1HNMR (CDCl$_3$), δ (ppm): 0.848-0.881 (t, 3H), 1.237-1.284 (t, 28H), 1.325-1.377 (q, 2H), 1.662-1.698 (t, 2H), 3.815-3.848 (t, 2H), 6.741-6.762 (d, 2H), 7.374 (s, 2H), 8.251-8.272 (d, 2H), 8.769 (s, 2H), 8.904-8.922 (d, 2H).

N$_6$: C$_{25}$H$_{24}$N$_4$O, FW = 396.5, yield: 39%. 1HNMR (CDCl$_3$), δ(ppm): 0.841-0.875 (t, 3H), 1.258-1.264 (d, Br$_2$, NaOAc

N$_{10}$: C$_{29}$H$_{32}$N$_4$O, FW = 452.6, yield: 73%. 1HNMR (CDCl$_3$), δ (ppm): 0.831-0.864 (t, 3H), 1.223-1.264 (d,

Figure 1. Structure of amphiphilic Eu(III) complexes.
12H), 1.308-1.345 (t, 2H), 1.632-1.702 (m, 2H), 3.790-3.822 (t, 2H), 6.720-6.741 (d, 2H), 7.360 (s, 2H), 8.221-8.242 (d, 2H), 8.762-8.770 (d, 2H), 8.893-9.12 (d, 2H).

N18: C33H40N4O, FW = 508.7, yield: 51%. 1H NMR (CDCl3), δ (ppm): 0.842-0.876 (t, 3H), 1.226 (s, 20H), 1.278-1.350 (m, 2H), 1.654-1.690 (t, 2H), 3.800-3.832 (t, 2H), 6.724-6.745 (d, 2H), 7.373 (s, 2H), 8.250-8.271 (d, 2H), 8.766 (s, 2H), 9.905 (s, 2H).

Synthesis of 2-m-pyridylmeth-anamido-5-phenyl-(1,3,4)-oxadiazole (PMA) 0.025mol m-pyridylethenyl-chlorine added into 0.025 mol 2-amino-5-(1,3,4)-oxadiazole (dissolved in pyridine and tetrahydrofuran) by stirring for 2 hours at 60°C in water bath and sediment was filtrated, washed by water and recrystallized in ethanol, vacuum dried and white crystal was got, yield 60%. C14H9N2O2, washed by water and recrystallized in ethanol, vacuum filtrated, washed and vacuum dried. Yield: 84%.

To the room temperature, 0.34 g yellow solid was got by cooling N18 into ethanol boiling for 0.5 hour. Cooling methanol) was dropped into 0.24 g PMA (dissolved in 20 ml ethanol, heated) and cooled to the room temperature, 0.34 g yellow solid was got by filtrated, washed and vacuum dried. Yield: 84%.

IR (KBr): Eu(PMA)3N6: 3055 (Ar-H); 2929 (C-H); 2853 (CH2); 1588 (phen:C=N); 1539 (C-C); 1253 (Ar-O); 764 (C-H).

Eu(PMA)3N10: 3061 (Ar-H); 2925 (C-H); 2853 (CH2); 1588 (phonic=N); 1539 (C-C); 1251 (Ar-O); 763 (C-H).

Eu(PMA)3N14: 3055 (Ar-H); 2924 (C-H); 2852 (CH2); 1588 (phonic=N); 1539 (C-C); 1252 (Ar-O); 763 (C-H).

Eu(PMA)3N18: 3058 (Ar-H); 2924 (C-H); 2852 (CH2); 1588 (phonic=N); 1539 (C-C); 1252 (Ar-O); 764 (C-H).

The surface pressure–area isotherms (at 20 (±0.5 °C)) and were left for 20 min for the solvent evaporation.

Table 1. Luminescence quantum yields data φ.

<table>
<thead>
<tr>
<th>Comple</th>
<th>λex(nm)</th>
<th>λem(nm)</th>
<th>Φ(%)</th>
<th>Life time(b/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(PMA)3N6</td>
<td>356</td>
<td>612</td>
<td>2.6</td>
<td>1.82</td>
</tr>
<tr>
<td>Eu(PMA)3N10</td>
<td>356</td>
<td>612</td>
<td>3.1</td>
<td>2.00</td>
</tr>
<tr>
<td>Eu(PMA)3N18</td>
<td>356</td>
<td>612</td>
<td>3.2</td>
<td>1.92</td>
</tr>
</tbody>
</table>

In tetrahydrofuran solution (Concentration: 2 × 10⁻⁶ mol·L⁻¹).
Figure 2. The π-A isotherms of europium complexes. (a) Eu(PMA)₃N₁₈; (b) Eu(PMA)₃N₁₄; (c) Eu(PMA)₃N₁₀; (d) Eu (PMA)₃N₆.

Table 2. Complex data at air/water interface.

<table>
<thead>
<tr>
<th>Number</th>
<th>A₀/nm²</th>
<th>Collapse pressure (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.58</td>
<td>42</td>
</tr>
<tr>
<td>b</td>
<td>0.65</td>
<td>47</td>
</tr>
<tr>
<td>c</td>
<td>0.62</td>
<td>40</td>
</tr>
<tr>
<td>d</td>
<td>0.63</td>
<td>42</td>
</tr>
</tbody>
</table>

about 0.58 A₀/nm² which is the smallest, which seems to be dominated by its longer chain in addition to the packed head group. These results reflect the effect of the structure of the molecules on their monolayer behaviors due to the large hydrophilic head group and long chains.

The data of monolayer LB film thickness measured with nkδ ~ 8000 v Thin Film Measurement Instrument and simulated theory molecule height were presented in Table 3, and then incline angle θ of molecule toward the substrate was calculated. According to the date of Tables 2, 3, the arrangement of the europium complexes were presumed that the part of ligands (PAM) and N₆,₁₀,₁₄,₁₈ coordinated with Eu³⁺ laid on horizontal direction on the water surface and the alkyl chains have certain orientation shown in Scheme 1.

3.2. LB Films Formation

The predominant feature of the UV spectra of the complexes under this investigation is the strong band occurring from 280 to 380 nm due to the π-π* type transition of the ligands associated with the conjugated transitions.

Table 3. Molecular arranging function in LB films.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Theoretical height/nm</th>
<th>Monolayer thickness/nm</th>
<th>Included angle θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(PMA)₃N₁₈</td>
<td>3.30</td>
<td>1.95</td>
<td>36.2</td>
</tr>
<tr>
<td>Eu(PMA)₃N₁₄</td>
<td>3.10</td>
<td>1.61</td>
<td>31.2</td>
</tr>
<tr>
<td>Eu(PMA)₃N₁₀</td>
<td>2.90</td>
<td>1.09</td>
<td>22.1</td>
</tr>
<tr>
<td>Eu(PMA)₃N₆</td>
<td>2.70</td>
<td>1.16</td>
<td>25.4</td>
</tr>
</tbody>
</table>

Scheme 1. Presumed arrangement of europium complexes on the water surface.

As an example, Eu(PMA)₃N₁₈ complexes absorptions in chloroform and in LB films were measured shown in Figure 3. Comparison of Eu(PMA)₃N₁₈ complex in LB films and in chloroform (Figure 3). Blue shift by 8 nm in LB films was observed compareing to the chloroform solution, which indicated that H aggregation was formed in LB films. The main peak of complex was at 287 nm in LB films attributed to super conjugated interaction and to π-π* electronic transfer of conjugated double bond of ligands. It was obvious that the distance of molecular in europium was shorter than that in chloroform, which resulted in stronger molecule interaction. Ligands were also packing orderly in LB films and played a great role in UV absorption. The similar results were also obtained for Eu(PAM)₃N₆, Eu(PAM)₃N₁₀ and Eu(PAM)₃N₁₄.

Depositions of the monolayers of europium complexes are mainly dependent on both the ligands and long chains. It is known that when using the same hydrophilicity for the head groups of the complexes, the film forming ability increased with increasing the length of chain. The traditional LB method is very useful for assembling Eu(PMA)₃N₆ with stronger hydrophilicity and hydrophobicity as multilayers, which may relate to the stronger interactions between two layers. For example, seen from the UV-vis spectra of multilayer europium complexes, for example (Figure 4), when the number of deposited layers increased, the absorption increased. Meanwhile, the absorbance at 288 nm of europium complexes is proportional to the number of layers deposited (inserted in Figure 4). The linearity indicated that the Eu (PMA)₃N₁₈ Langmuir film could be transferred onto the substrate successfully forming regular multilayers. Other complexes showed the similar results for Eu(PAM)₃N₆, Eu(PAM)₃N₁₀ and Eu(PAM)₃N₁₄.
3.3. Fluorescence Spectra

The emission spectra of all the multilayer europium complex LB films were measured. We could observe that all of them could give strong emission intensity. Emission spectra for 100-layer LB films of Eu(PAM)3N18 1), Eu(PAM)3N14 2), Eu(PAM)3N10 3) and Eu(PAM)3N6 4) were obtained shown in Figure 5. The emission spectra of Eu(PAM)3Nn (n = 18, 14, 10, 6) of 100-layer LB films (λex = 372 nm) gave evident Eu(III) characteristic peaks at 582, 591, 612 and assignable to 5D0 → 7Fj (j = 0 - 2), respectively, in which hypersensitive emission (j = 2) is expected to be more sensitive to the ionic environment in terms of shifts in peak position as well as the relative intensity.

The hypersensitive 5D0 → 7F2 transition is predominant in these complexes, indicating that Eu3+ may lie in symmetry sites without inversion center [32]. Influenced by strong frequency doubling peak (λem = 612 nm), the excitation spectrum was not obvious before 350 nm (not shown here). Monochromacity factor was shown in Table 4 for an intensity ratio of 5D0 → 7F2 to 5D0 → 7F1 emission. The value of Eu(PAM)3N18 was lower than that of other complexes, which might be influenced by coordinate environment changing in LB films and molecules were packing tightly, which resulted in local symmetry of Eu(III) centre ion increased in LB films.

Generally, monochromacity factor of Eu(PAM)3N6 and Eu(PAM)3N10 were better, while monochromacity factor of Eu(PAM)3N14 and Eu(PAM)3N18 were lower. It was considered as molecular packing neatly for Eu(PAM)3N14 and Eu(PAM)3N18 in LB films and a small part of energy was bound. So it might, to some extent, inhibit energy to transfer from ligands to center ion. More explanation would be given by AFM analysis.

Another important result of this study is the influences of the asymmetry of PMA ligands on the emissions of the complexes. It is found that the emission of 5D0 → 7F0 and 5D0 → 7F2 are not splitting which occurs in other studies [33].

Considering that 5D0 → 7F0 is strictly forbidden in a regular octahedral field, the emission from 5D0 → 7F0 in LB films suggests the influence of the closely packed structure on the asymmetry of the ligands surrounding the metal ions. The differences in the emission spectra for these complexes in LB films suggest that the emissions of the complexes with asymmetrically substituted ligands are little influenced by co-ligand with different length chains.

3.4. Energy Transfer between PAM and Europium(III)

In an effort to demonstrate the energy transfer process, the phosphorescence spectra of the complexes Gd(PAM)3-(H2O)2 was measured at 77 K for triplet energy level data of the ligand PAM. Since the lowest excited state 4P7/2 of Gd(III) ion is too high to accept energy from a ligand, the data obtained from the phosphorescence spectra of the complexes actually reveal the triplet energy level of the corresponding ligand [34]. The triplet state energy (2ππ*) levels of PAM based on our measurement was found to be 20 200 cm⁻¹ (495 nm). The triplet energy (1ππ*) levels of DBM (20 520 cm⁻¹), bpy (22 900 cm⁻¹) and phen (22 100 cm⁻¹) were taken from the literatures [35,36].

Generally, the sensitization pathway in luminescent europium complexes consists of the excitation of the ligands from the ground state to their excited singlet
Figure 5. Fluorescence spectra of complex LB films emission spectra of Eu(PAM)$_3$N$_{18}$ (a), Eu(PAM)$_3$N$_{14}$ (b), Eu(PAM)$_3$N$_{10}$ (c), Eu(PAM)$_3$N$_{6}$ (d).

Table 4. Complex emission spectra.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Layers number</th>
<th>$^5$D$<em>0$→$^1$F$</em>{0}$</th>
<th>$^5$D$<em>0$→$^1$F$</em>{1}$</th>
<th>$^5$D$<em>0$→$^1$F$</em>{2}$</th>
<th>Monochromacity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(PMA)$<em>3$N$</em>{18}$</td>
<td>100</td>
<td>582</td>
<td>591</td>
<td>612</td>
<td>3.85</td>
</tr>
<tr>
<td>Eu(PMA)$<em>3$N$</em>{14}$</td>
<td>100</td>
<td>580</td>
<td>591</td>
<td>612</td>
<td>4.23</td>
</tr>
<tr>
<td>Eu(PMA)$<em>3$N$</em>{10}$</td>
<td>100</td>
<td>584</td>
<td>591</td>
<td>612</td>
<td>6.18</td>
</tr>
<tr>
<td>Eu(PMA)$<em>3$N$</em>{6}$</td>
<td>100</td>
<td>579</td>
<td>591</td>
<td>612</td>
<td>5.24</td>
</tr>
</tbody>
</table>

states, subsequent intersystem crossing of the ligands to their triplet states, and the energy transfer from the triplet state of the ligand to $^5$D$_J$ manifold of the Eu$^{3+}$ ion, following by internal conversion to the emitting $^5$D$_0$ state; finally the Eu$^{3+}$ ion emits when the 4f electrons undergo a transition from the excited state of $^5$D$_0$ to the ground state [37]. Moreover, the electron transition from the higher excited states, such as $^5$D$_3$ (24 800 cm$^{-1}$), $^5$D$_2$ (21 200 cm$^{-1}$), and $^5$D$_1$ (19 000 cm$^{-1}$), to $^5$D$_0$ (17 500 cm$^{-1}$) becomes feasible by internal conversion, and most of the photophysical processes take place in this orbital. Consequently, most europium complexes give rise to
typical emission bands at 581, 593, 614, 654, and 702 nm corresponding to the deactivation of the excited state \(^5\text{D}_0\) to the ground states \(^7\text{F}_J\) \((J = 0 - 4)\). Therefore, matching the energy levels of the triplet state of the ligands to \(^5\text{D}_0\) of Eu\(^{3+}\) is one of the key factors that affect the luminescent properties of the europium complexes.

Based on the above experimental results, the triplet energy level of PAM (20 200 cm\(^{-1}\)) is obviously higher than the \(^5\text{D}_0\) level (17 500 cm\(^{-1}\)) of Eu\(^{3+}\), and its energy gap \(\Delta E(\pi\pi^* - 5\text{D}_0)\) between ligand and metal-centered levels is too high to allow an effective back energy transfer. According to Latva’s empirical rule \([27,38]\), an optimal ligand-to-metal energy transfer process for Eu\(^{3+}\) needs \(\Delta E(\pi\pi^* - 5\text{D}_0) > 2500\) cm\(^{-1}\) and hence the energy transfer process is effective for these complexes.

3.5. Surface Topography of Europium Complexes Monolayer

Monolayer assemblies of these complexes were fabricated by the LB method and transferred onto substrate with a vertical lifting technique. Monolayer morphology of these amphiphilic Eu(III) complexes with different long chains has been investigated by AFM method, that showed that the structure for the monolayers of Eu complexes was closely related to the length of long chains. Qian et al investigated the monolayer assemblies of some europium complexes with the \(\alpha\)-diketonate ligand thiényltrifluoroacetone and concluded that the closely packed structures of the complexes have some influences on the emissions of the lanthanoid ions, especially for the Eu and samarium complexes \([22]\). Therefore, we try to insight the relationship between their arrangement and fluorescence properties of europium complexes.

The AFM images of Eu complexes monolayer were shown in Figure 6. The aggregation of Eu(PMA)\(_3\)N\(_6\) LB films were flat and smooth (Figure 6(a)), having directionality and orientation without deficiency. Explained from molecular level, we thought that molecules arranging regularly in LB films and the distance between molecules in LB films became shorter, which made the \(\pi-\pi^*\) interaction strengthened. It illustrated that the surface pressure in LB formation procedure was supplied a comfortable force which made the film resist deformation to form stable monolayer. In order to observe surface aggregations in LB films, AFM images were amplified to 500 nm \(\times\) 500 nm (Figure 6(b)), in which we could see loose surface topography in the Eu(PMA)\(_3\)N\(_6\) film. The molecules arrangement was supposed in a loose state, in which there is a little distance between molecules.

In the case of Eu(PMA)\(_3\)N\(_{10}\), Eu (PMA)\(_3\)N\(_{14}\) and Eu (PMA)\(_3\)N\(_{18}\) “Hole coral” was observed in the Eu(PMA)\(_3\)N\(_{10}\) film AMF image (Figures 7(a), (b)). The probable orientation of Eu(PMA)\(_3\)N\(_{10}\) was that there are some overlapping parts among Eu(PMA)\(_3\)N\(_{10}\) molecules.

We also could find the aggregates of the Eu(PMA)\(_3\)N\(_{14}\) films and the Eu (PMA)\(_3\)N\(_{18}\) films were packing neatly and showed “columnar shape” and “tetragonal shape” showing more condense structure in Figures 8(a), (b) and Figures 9(a), (b), in which there are more overlapping parts among molecules. It leads the part energy absorbed to transfer to ligands instead of transferring to centre ion. Arrangement way in the Eu(PMA)\(_3\)N\(_6\) film and in the Eu(PMA)\(_3\)N\(_{10}\) film were packing more loosen
than that of other films. We thought that energy obtained from certain wavelength light could transfer more easily from ligands to center ion in the Eu(PMA)$_3$N$_6$ LB films and in the Eu(PMA)$_3$N$_{10}$ LB films which led to higher monochromaticity. It was obvious that monochromaticity had some special relationship with the arrangement of molecular in film. At the same time, we can conclude that if we arrange the orientation of molecule in proper certain way with LB technology, energy transferring from ligand to centre ion can be efficiently achieved and strong luminescent intensity and Eu(III) center ion emission monochromaticity be obtained. It is interesting that the molecular with looser arrangement in LB films has better monochromacity, which illustrated that energy might transferred more easily in loosen structure films.

4. Conclusions

A series of new amphiphilic Eu(III) complexes were synthesized and were fabricated into ordered LB films. All of these amphiphilic europium(III) complexes could form stable Langmuir film at air/water interface and
could be transferred onto hydrophilic quartz and mica substrates. In order to investigate relation between fluorescence properties and the arrangement of molecular in LB films, surface topography of monolayer and fluorescence properties of LB films were investigated by fluorescence spectroscopy and atomic force microscopy (AFM), respectively. Results showed that order structure of LB films could give strong Eu$^{3+}$ characteristic emission spectra.

Eu(PMA)$_3$N$_6$ and Eu(PMA)$_3$N$_{10}$ gave higher monochromacity factor than that of other complexes films because of the loosen structure of LB films. We thought that the loosen structure of LB films might transfer energy from ligands to center ion more easily, which lead to better monochromacity factors.

5. Acknowledgments

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6. References


[27] C. Hiort, P. Lincoln and B. Norden, “DNA Binding of \( \Delta \) and \( \lambda \) of \( \text{Ru}(\text{phen})_2(2\text{DPPZ})_2^+ \),” Journal of the American Chemical Society, Vol. 115, No. 9, 1993, pp. 3448-3454. doi:10.1021/ja00062a007


[33] D. J. Qian, K. Z. Yang, H. Nakahara and K. Fukuda, “Monolayers of Europium Complexes with Different Long Chains and β-Diketone Ligands and Their Emissive


