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LANGMUIR-BLODGETT FILMS OF A SERIES OF NEW FLUORESCENT TERNARY EUROPIUM(III) COMPLEXES

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Three europium complexes 1-methyl-4-octadecylpyridinium tetrakis(α -thenoyl trifluoroacetonato) europium(III), tris(α -thenoyl trifluoroacetonato) mono-(9-(4-hexadecylanilino)-4,5-diazafluorene) europium(III), and tris(α -thenoyltrifluoro acetonato) mono(2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline) europium(III) have been newly synthesized. They were capable of forming stable Langmuir films on pure water subphase(pH 5.6, 18 °C) with collapse pressures of 39.0, 50.0 and 20.5 mN/m, respectively. Langmuir-Blodgett films of these complexes have been prepared and studied by surface pressure-area isotherms, ultraviolet, fluorescent spectroscopy, fluorescent lifetime measurements and second-harmonic generation. Copyright © 1996 Published by Elsevier Science Ltd

Keywords: A: thin films, D: optical properties, E, luminescence and nonlinear optics.

1. INTRODUCTION

Europium(III) complexes with some 1, 3-diketones have assumed considerable importance because of their practical applications as potential laser materials,^[1] supersensitive determination of lanthanides photometrically,^[2] fluorescent probe for the structures of biomacromolecules,^[3] luminescent labels in immunology, [4] display devices [5,6] and agriculture in plastic membranes. Among them, europium complexes with a-theonyltrifluoroacetone(HTTA) or β -naphthyltrifluoroacetone (HNTA) have been attracted much attention due to their excellent fluorescent characteristics. Recently, some amphiphilic complexes of this kind have renewed interests in the preparation of Langmuirblodgett(LB) films^[7-9] due to their potential applications in electroluminescent and luminescent

devices, and microcavity.^[10] However, the problems arisen from very loose packing of the europium complex in the film^[9] and poor film-forming property remain to be resolved. Although the addition of auxiliary film-forming materials such as stearic acid could improve film-forming property of the materials, this had potential phase separation and had a negative effect on fluorescent characteristics.^[7,8] In this communication, we wish to report the three new europium-TTA complexes which have good filmforming property without the addition of any auxiliary film-forming materials. Also, interestingly, one of the complexes without long alkyl chain may be interested to be used in electronic devices because the presence of alkyl layers in LB films usually have poor vertical conduction.

2. EXPERIMENTAL

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Materials. Molecular structures of three europium

complexes used here are shown in Fig.1. 1-methyl-4octadecylpyridinium tetrakis(a-thenoyltrifluoroacetonato)europium (III) (MOPEu(TTA)4) was synthesized according to the method described for analogues.^[8] Anal. Calcd for C56H60F12NO8S4Eu: C, 46.6; H, 4.16; N, 0.97%. Found: C, 46.9; H, 4.20; N, 1.03%. Tris(a-thenoyltrifluoroacetonato)mono(9-(4-hexadecylanilino)-4, 5-diazafluorene)europium(III) (Eu(TTA)3 HDF) was synthesized according to following two steps: (a) the synthesis of 9-(4hexadecylanilino)-4, 5-diazafluorene(HDF): a mixture of 1.05 mmol of 4, 5-diazafluorendione^[11] and 1 mmol of 4-hexadecylaniline in 20 ml of ethanol was refluxed for 1 h in presence of several drops of 6 mol/l of hydrochloric acid as the catalyst. The precipitate formed on cooling was filtered and recrystallized in ethanol-water to afford yellow product. Anal. calcd for C33H43N3: C, 82.33; H, 8.94; N, 8.73%. Found: C, 82.19; H, 9.03; N, 8.52%. (b) the synthesis of (Eu(TTA)₃·HDF): A solution of 1 mmol of Eu(TTA)3. 2H2O[12] and 0.98 mmol of HDF in 30 ml toluene was refluxed under stirring for 1 h. Most of the solvent was driven off under reduced pressure in a water bath and then 10 ml of petroleum ether (30-60 °C) was added. The precipitate formed on cooling in a refrigerator was filtered under suction and recrystallized in toluene-petroleum ether(30-60 °C). Anal. Calcd for C57H55F9N3O6Eu : C, 52.78; H, 4.24; N, 3.24%. Found: C, 52.70; H, 4.29; N, 3.40%. IR(KBr): 576(w); 640(w); 680(w); 721(w); 762(w); 799(m); 920(w); 1064(w); 1142(s); 1188(s); 1231(m); 1248(m); 1308(vs); 1356(m); 1413(s); 1461(m); 1508(m); 1539(s); 1581(m); 1602(vs);1625(m); 2874(m); 2930(m); 2959(m) cm⁻¹.Tris(α -thenoyltrifluoroacetonato)mono(2,9-dimethyl-4,7-diphenyl-1,

10-phenanthrolinc)europium(III) (Eu(TTA)₃· phen) was synthesized according to a similar method described for Eu(TTA)₃· HDF. Anal. Calcd for $C_{50}H_{32}F_{9}N_{2}O_{6}S_{3}Eu: C, 51.1; H, 2.72; N, 2.38\%$. Found: C, 51.9; H, 2.80; N, 2.48%.

Film Deposition. The europium complexes were ultrasonically dissolved in CHCl₃ and were spread onto pure water subphase (pH 5.6, 20 °C) with a British NIMA Langmuir-Blodgett trough. After vaporization of CHCl₃, the surface pressure-area (π -A) isotherms were recorded. At a constant π (10 mN m⁻¹ for Eu(TTA)₃· phen, 15 mN m⁻¹ for MOPEu(TTA)₄ and 20 mN m⁻¹ for Eu(TTA)₃· HDF), the floating monolayers of were transferred in Y-

 $Eu(TTA)_3$ ·HDF (b) and MOP·Eu(TTA)_4 (c)

Fig. 1 Molecular structures of Eu(TTA)₃·phen (a),

type mode onto hydrophilic quartz substrates^[13] at a dipping speeds of 5 mm min⁻¹.

Spectroscopic Measurements. Apparatus and methods of ultraviolet and fluorescent spectral measurements and Second-harmonic generation(SHG) from the monolayers are same as those described previously.^[14,15] The details of the experimental and data treatment methods for fluorescence lifetime determination have been published previously.^[16]

3. RESULTS AND DISCUSSION

π-A Curves. π-A curves for the complexes are given in Fig. 2. The film-formig parameters of these materials are tabulated and compared with their analogues in Table 1. As can be seen from both the Fig. 1 and Table 1, the complexes Eu(TTA)₃· HDF and MOPEu(TTA)₄ have higher collapse pressures (CP) than other congeners. The π-A curve of Eu(TTA)₃· HDF steeply rises as the compression of the monolayer and collapses at a very high π over 40 mN m⁻¹. While Eu(TTA)₃· phen also has relatively steep π -A curve but with a very low CP of ca. 20 mN m⁻¹. HDPEu(TTA)₄ (HDP=hexadecylpyridinium) could not form stable Langmuir film alone,^[7] but the





Fig. 2 The π -A isotherms of Eu(TTA)₃ phen (a), Eu(TTA)₃ HDF (b) and MOP Eu(TTA)₄ (c)

film formation was gained when the HDP⁺ was replaced by more hydrophobic MOP⁺. However, the molecular area of MOPEu(TTA)4 is much more larger than the calculated area (0.55 nm^2) of the complex anion Eu(TTA)4⁻, indicating loose packing or a much tilt arrangement of the MOP⁺ in the monolayers.

UV Spectra. On comparing the ultraviolet spectra of the 3-layer films with those of corresponding CHCl₃ solutions (Figs. 3 and 4), one find both the peak positions and relative intensities of the films differ from corresponding CHCl₃ solutions, This most probably due to the existence of aggregations in the films due to highly ordered and closely packed structure of the films. It should be noteworthy that this phenomenon may be the common feature of trifluoroacetyl-containing film-forming materials^[7-9, 17] but was not observed in the films of other lanthanide- β -diketonate complexes^[15,18]. The



Fig. 3 UV spectra of $Eu(TTA)_3$ ·phen (a), $Eu(TTA)_3$ ·HDF (b) and MOP·Eu(TTA)_4 (c) in CHCl₃



Fig. 4 UV spectra of the films of $Eu(TTA)_3$ phen (a), Eu(TTA)_3 HDF (b) and MOP Eu(TTA)_4 (c)

existence of strongly electron-withdrawing trifloroacetyl may be main reason of strong intermolecular interaction.

Fluorescent Properties As shown in Fig. 5, the excitation spectra for the monolayer films of HOPEu(TTA)₄, Eu(TTA)₃. phen and Eu(TTA)₃. HDF, obtained at an emission wavelength of 614, 614 and 624 nm respectively, differ considerably each other. Fluorescent spectra for the films of Eu(TTA)₃. HDF, HOPEu(TTA)₄ and Eu(TTA)₃. phen, excited at 360, 350 and 280 nm respectively, are given in Fig. 6. The fluorescent data of the films are given in Table 2. Each of luminescence spectra for the LB films of the three complexes shows five characteristic emission peaks of Eu(III) complex at ca.580, 592, 614, 656 and



Fig. 5 Fluorescence excitation spectra of the monolayers: Eu(TTA)₃·phen (a), Eu(TTA)₃·HDF (b); MOP·Eu(TTA)₄ (c)

Table 1. The film-forming parameters

materia	al* C.P. (mN/m)	$A_{\pi \rightarrow 0}$ (nm ²) (n	slope nN m ⁻¹ nm	ref. -2)
	39	1.16	58.8	this work
b	50	0.42	342	this work
с	21	0.81	94.7	this work
d	25	1.25	143	14
e	15	1.14	15.3	7

*a, MOPEu(TTA)4;b,Eu(TTA)3 · HDF;Eu(TTA)3 · phen; d, HDPEu(PMBP)4;e, HDPEu(TTA)4

Table 2.	Fluorescent	data of	monolayers
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LB films*	· λ _{ex} (nm)	$\lambda_{em} (nm) of$ $5D_0 \rightarrow {}^7F_2$	monochromaticity**				
(relative intensity)							
a	350	614(6.2)	17.6				
b	360	624(0.7)	3.8				
с	290	614(150)	21.8				
d	350	613(<0.01)	5.0				
e ·	350	613(<0.1)	14.9				

*a, MOPEu(TTA)4;b, Eu(TTA)3· HDF;c, Eu(TTA)3· phen; d, HDPEu(PMBP)4;e, HDPEu(TTA)4: stearic acid=1:4 **I($^{5}D_{0} \rightarrow ^{7}F_{2}$)/I($^{5}D_{0} \rightarrow ^{7}F_{1}$)

703 nm, respectively. These peaks are due to transitions within the 4f⁶ electron shell and assigned to five energy level transitions from ⁵D₀ metastable state to terminal levels, respectively:⁷F_j(j=0, 1, 2, 3 and 4). More clearly, the fluorescent intensity of induced electronic dipolar transition ⁵D₀ \rightarrow ⁷F₂ is predominant in each of the spectra. One use the ratio of electronic dipolar transition intensity I(⁵D₀ \rightarrow ⁷F₂) to magnetic dipolar transition I(⁵D₀ \rightarrow ⁷F₁) intensity as the standard of monochromaticity and found that both the films of HOPEu(TTA)₄ and Eu(TTA)₃. phen have good monochromaticity. However, ⁵D₀ \rightarrow ⁷F₂ peak was split into two peaks at 612 and 624 nm in the spectrum of Eu(TTA)₃. HDF film and this split was not observed in the CHCl₃ solution spectrum. It



Fig. 6 Fluorescence emission spectra of the LB films: (a) Eu(TTA)₃ phen, $\lambda_{\rm EX} = 290$ nm; (b) Eu(TTA)₃.HDF, $\lambda_{\rm EX} = 290$ nm; (c) MOP Eu(TTA)₄, $\lambda_{\rm EX} = 350$ nm.

should be also emphasized that the complex Eu(TTA)₃ HDF has the best film-forming properties but very poor fluorescent properties with nearly totally quenched fluorescence and greatly decreased monochromaticity. This effect may be due to the energy loss and thermal deactivity of the excitation state caused by strong vibration of alkyl chain attached to the complex, and also a slight distortion in the symmetry of the Eu complex. As is clear from Vol. 98, No. 12

Table 2, the fluorescent intensity order of the films is Eu(TTA)3. phen> MOPEu(TTA)4> Eu(TTA)3. HDF inconsistent with solution intensity order MOPEu(TTA)₄> Eu(TTA)₃· phen≥ Eu(TTA)₃· HDF. The abnormally large ${}^{5}\text{D0} \rightarrow {}^{7}\text{F2}$ intensity of the film of Eu(TTA)3. phen may associate with microcrystal formation on the substrate. Fluorescent lifetime of CHCl3 solutions for Eu(TTA)3 phen and MOPEu(ITA)₄ were determined by phasemodulation method to be 215 and 485 µs, respectively, are slightly high than 188 us for the film of Eu(TTA)3 phen and 372µs for the film of MOPEu(TTA)₄. However, the fluorescent lifetime of Eu(TTA)3. HDP could not be properly determined due to its weak fluorescent intensity. These results show that the fluorescent characteristics of the materials are highly sensitive to the compositions and structures and supramolecular assembling of the materials.

SHG. SHG from the monolayer films was made in transmission with 1.064 μ m Nd:YAG fundamental light. The film of MOPEu(TTA)4 showed appreciable SH signals although not very large. However, the films of Eu(TTA)3 · HDP and Eu(TTA)3 · phen show no detectable SH signals. Clearly, the donor- π acceptor structure of the counter cation MOP⁺ is

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responsible for the SH signals. According to the literature method^[18,19], the values of susceptibility $\chi^{(2)}$, second-order molecular hyperpolarizability β and tilt angle Φ of the chromophore with respect to the surface normal of the film were derived to be 6.1×10^{-8} esu, 2.2×10^{-29} esu and 75.5° . The relatively small β value compared with typical second-order nonlinear optical materials, such as hemicyanine,^[15] is responsible for the weak electron-donating ability of methyl. The large tilt angle may count for the large molecular area of the MOPEu(TTA)4.

4. SUMMARY

We have successfully prepared three fluorescent LB films of pure europium complexes. Highly ordered structures of the films greatly affect their UV spectra and fluorescent characteristics. This study may provide a way for developing photochemical devices of molecular dimension.

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