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Optical properties of the highly ordered Langmuir–Blodgett film of a strongly luminescent Eu(III) complex

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Abstract

A novel amphiphilic europium(III) complex, tris(α-thenoyltrifluoroacetonato)mono(1-octadecyl-2-(2-pyridyl)benzimidazole) europium(III) (Eu(TTA)$_3$(L18)), was newly synthesized. It formed stable monolayer film on pure water subphase with a limiting area of 0.52 nm^2 per molecule. Multilayer Langmuir–Blodgett (LB) film was built onto hydrophilic quartz substrate and characterized by ultraviolet and emission spectroscopy, and low-angle x-ray diffraction analyses. Quite highly ordered structure of the LB film was revealed by the appearance of five sharp Bragg diffraction peaks with half-width at full maximum for the strongest one being only 0.16 Å.

Keywords: Europium complex; Spectroscopy; Langmuir–Blodgett films

1. Introduction

Langmuir–Blodgett (LB) technique has long been recognized as one of the most powerful tools of making advanced thin film materials with highly ordered lameller structure [1,2]. The functional molecules oriented in such a supramolecular environment would bring about fascinating functions which may be distinct from bulky materials. Eu(III) complexes with suitable organic ligands show strong ligand-sensitized Eu(III) characteristic luminescence with excellent monochromacity of bandwidth of typically ca. 10 nm, and long lifetimes up to several milliseconds [3]. These characteristics make them good candidates for advanced optoelectronic materials [4]. The introduction of fluorescent Eu(III) complexes into LB films pioneered by Kuhn in 1971 [5], have recently renewed interest by our group [6] and others [7], aimed at investigating the correlation of film formation and fluorescence behaviors of Eu(III) complexes with molecular and film structures. Although LB technique is well known for making highly ordered film structure characterized by the appearance of regular x-ray diffraction patterns at low-angle region [1], to the best of our knowledge, highly ordered film structure has never been achieved for fluorescent Eu(III) complex LB films to date. Here we wish to report on the highly ordered LB film made of a novel amphiphilic Eu(III) complex and its optical properties.

2. Experimental section

2.1. Synthesis

Synthetic route to the amphiphilic Eu(III) complex is given in Scheme 1. Synthetic details are given as follows.

2.1.1. Synthesis of 2-(1-octadecylbenzimidazol-2-yl)pyridine (L18)

Under N$_2$, a suspension of NaH (50 mg, 60% dispersed in mineral oil) prewashed with anhydrous hexane, and 2-benzimidazole (0.21 g, 1.0 mmol) in 15 ml of anhydrous *N*,*N*′-dimethylformamide was stirred at the room temperature for 1 h. Bromooctadecane (0.33 g, 1.0 mmol) was then added and the mixture was refluxed for 24 h. After cooling to the room temperature, the solution was filtered and the solvent was driven off under reduced pressure. The crude product was chromatographed on silica gel (CH$_2$Cl$_2$:CH$_3$OH, v/v 9:1). MP 63–64 °C. Anal. calcd. for C$_{30}$H$_{45}$N$_3$: C, 80.73; H, 10.10; N, 9.38. Found: C, 80.54; H, 10.07; N, 9.40. ^{1}H NMR: 0.878 (t, 3H, –CH$_3$); 1.30 (m,

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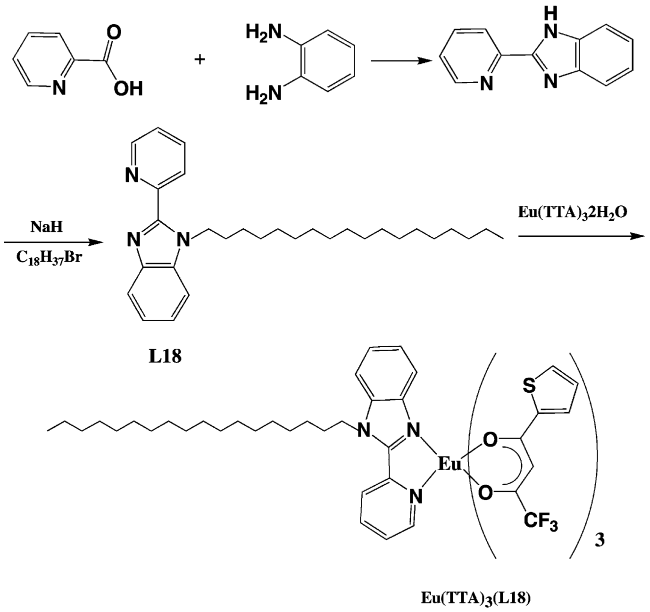

Scheme 1. Synthetic route to the Eu(III) complex.

30H, –(CH_2)$_{15}$); 1.87 (q, 2H, –CH_2); 4.82 (t, 2H, –CH_2); 7.32 (m, 3H, aromatic); 7.45 (d, 1H, aromatic); 7.84 (m, 2H, aromatic); 8.41 (d, 1H, aromatic); 8.68 (m, 1H, aromatic).

2.1.2. *Synthesis of tris(α-thenoyltrifluoroacetonato)mono(1-octadecyl-2-(2-pyridyl)benzimidazole)europium(III) (Eu(TTA)$_3$(L18))*

Eu(TTA)$_3$2H_2O (0.213 g, 0.25 mmol) and L18 (0.112 g, 0.26 mmol) were refluxed in 15 ml of toluene for 1 h. The solvent was driven off under reduced pressure in a water bath. The residue was twice recrystallized from CH_2Cl_2–hexane. Anal. calcd. for $C_{54}H_{57}O_6F_9S_3N_3Eu$: C, 51.13; H, 4.42; N, 3.31. Found: C, 51.32; H, 4.51; N, 3.32. MP 95–98 °C. IR (KBr): 2925 (m); 2854 (w); 1626 (s); 1602 (vs); 1538 (s); 1505 (m); 1469 (m); 1413 (s); 1356 (m); 1308 (vs); 1246 (w); 1229 (w); 1189 (s); 1143 (vs); 1062 (w); 787 (m); 744 (w); 718 (w); 642 (w); 581 (w).

2.2. *Spectroscopy*

Ultraviolet spectra were obtained with a Shimadzu 240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Infrared spectra were recorded on a 7199 B FT-IR system. Low-angle x-ray diffraction instrumentation was same as before [8].

2.3. *LB film preparation*

A chloroform solution (1.46 mg/ml) of the Eu(III) complex was spread onto pure water subphase (purified by EASY pure RF compact ultrapure system, $R \sim 18\,\mathrm{M\Omega}$) in a Nima Langmuir trough and was left for 15 min for the solvent evaporation. The surface pressure–area isotherm was then recorded at a barrier compression rate of 80 $\mathrm{cm^2}$/min. Compression–expansion (CE) isotherms were obtained by immediately expanding the monolayer after the barrier hit to the target pressures. The LB films were deposited in a Y-type mode onto hydrophilically treated quartz substrates [9] at a deposition rate of 5 mm/min.

3. Results and discussion

3.1. *Surface pressure–area isotherm*

Fig. 1a shows the surface pressure–area isotherm of the complex on pure water subphase. From a molecular area of 0.63 $\mathrm{nm^2}$ per molecule, surface pressure appeared and underwent a moderately steep rise until 23 $\mathrm{mN\,m^{-1}}$ followed by a phase transfer. Extrapolation of the linear region of π–A curve with surface pressures lying from 9.5 to 23 $\mathrm{mN\,m^{-1}}$ to a zero surface pressure, a limiting molecular

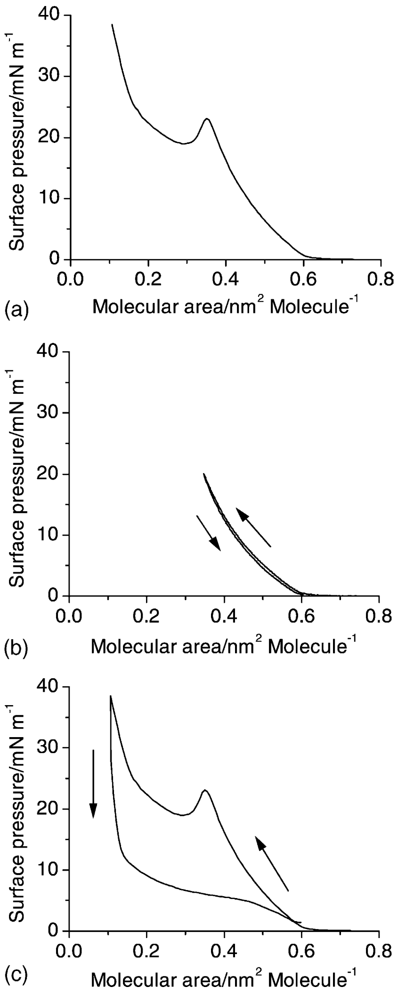

Fig. 1. Surface pressure–area isotherm of Eu(III) complex on pure water subphase (a); CE isotherms recorded at reversal surface pressures of 10 $\mathrm{mN\,m^{-1}}$ (b) and 38 $\mathrm{mN\,m^{-1}}$ (c).

area of 0.52 nm^2 per molecule was derived and is consistent with 0.63 nm^2 per molecule observed for Eu(TTA)$_3$phen (phen = 1,10-phenanthroline) [7a] and projection area of 0.60 nm^2 obtained based on molecular modeling, indicative of formation of monolayer. This is also supported by the fact that CE isotherms (Fig. 1b) at a reversal surface pressure of 10 mN m^{-1} did not show any appreciable hysteresis. The second linear region of step rise in surface pressure with decreasing molecular areas occurred from surface pressures of 25–38 mN m^{-1}, corresponding to a limiting area of 0.26 nm^2. Several possibilities may account for much decreased molecular area observed for the new phase: the formation of bilayer or multiplayer film; the formation of aggregates; and the changes in molecular orientations [8]. CE curves (Fig. 1c) obtained at a reversal surface pressure of 38 mN m^{-1}, showed significant hysteresis, supporting the formation of aggregates [9]. This conclusion was also verified by UV and emission spectroscopy which will be discussed below.

3.2. Film formation properties and UV spectra

When LB films were transferred at 12 mN m^{-1}, a surface pressure lying from 10 to 20 mN m^{-1} for monolayer film formation, only monolayer LB films could be effectively transferred onto hydrophilic quartz substrates with transfer ratios close to unity, subsequent multilayer deposition failed, regardless of various efforts in changing deposition parameters, e.g. deposition rates and drying time of the films after taking out of the water surface. However, multilayer films could be built at high surface pressures, e.g. 30 mN m^{-1} at which the complex is highly aggregated as evidenced by CE experiments discussed above. However, a plot of absorbance at 315 nm against number of layers deposited did not give a straight line through the origin. The deviation from Lamber–Beer law is due in part to inhomogeneous deposition of the LB films, but most probably to the aggregates formation. As shown in Fig. 2, the complex in CHCl$_3$ exhibited a strong wide absorption band centered at 343 nm and a weak one at 268 nm which are attributable to superstition of TTA$^-$ and L18-centered $\pi \rightarrow \pi^*$ transitions. The UV-Vis spectrum of a monolayer LB film transferred at a surface pressure of 12 mN m^{-1} gave an absorption band at 308 nm which is much narrowed in bandwidth and blue-shifted by 35 nm compared to the chloroform solution. The UV spectral differences observed between the solution and the film may result form highly ordered molecular arrangement in the film [6c,6d,7b]. The complex in the LB film transferred at 30 mN m^{-1}, exhibited a UV absorption peak at 316 nm which is red-shifted by 8 nm relative to the film prepared at 12 mN m^{-1} and characterized by a shoulder at 338 nm. The red shift and new shoulder observed for the film prepared at 30 mN m^{-1} compared to the monomer film are ascribed to J-aggregate formation [8].

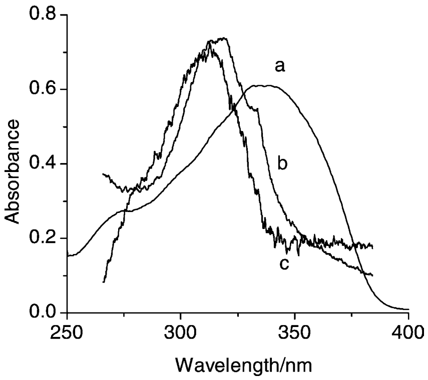

Fig. 2. UV spectra of Eu(III) complex in CHCl$_3$ (a); LB films deposited at 30 mN m^{-1} (b) and 12 mN m^{-1} (c).

3.3. Emission spectra

Excitation and emission spectra for compressed complex powder, LB films deposited at both 12 and 30 mN m^{-1} are compared in Figs. 3 and 4, respectively. The complex powder gave a structureless broad excitation spectrum characteristic for powder sample due to the light scattering caused by inhomogeneous surface and particle distribution [10]. The film prepared at 12 mN m^{-1} exhibited a defined excitation spectrum centered at 324 nm with a shoulder at 366 nm. The film prepared at 30 mN m^{-1} showed a defined excitation spectrum without a low-energy shoulder. The maximum excitation wavelength locates at 330 nm which is red-shifted by 6 nm compared to the film prepared at 12 mN m^{-1}, similarly to the observation by UV spectroscopy discussed above. The complex powder emitted strong red light to the naked eye when excited by ultraviolet light. The emission spectrum for the powder obtained by maximum excitation at 300 nm showed five evident Eu(III) characteristic peaks at 579, 592, 612, 652 and 701 nm, and assignable to $^5D_0 \rightarrow {}^7F_j$ ($j = 0$–4), respectively. The emission is highly monochromic as presented by a monochromacity factor of 11.0 for an intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ emission. The monolayer LB film deposited at 12 mN m^{-1} showed almost same five emission peaks as pointed out above for the complex powder. The monochromacity factor for the film is reduced to 7.3, probably due to the increase in local symmetry of Eu(III) ion in the film environment [11]. The LB film deposited at 30 mN m^{-1}, however, gave a greatly quenched emission with the strongest $^5D_0 \rightarrow {}^7F_2$ emission at 612 nm hardly observable. It is interesting to note that a very broad-band emission appeared at 780 nm along with the weak Eu(III) emission. The excitation spectrum (Fig. 3d) for the wide-band emission is almost same as that for the Eu(III) emission (Fig. 3c) in the same film sample. The emission for the broad band is thus ascribed to that of aggregate which resulted in quenching in Eu(III) emission at 612 nm observed for the film prepared at 30 mN^{-1}.

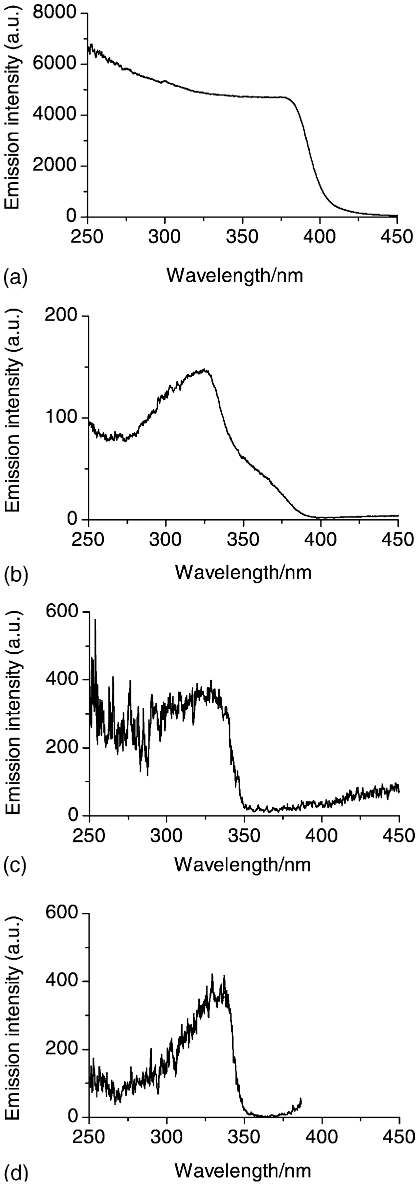

Fig. 3. Excitation spectra of Eu(III) complex in compressed powder (a), $\lambda_{em} = 612$ nm; in LB film deposited at 12 mN m^{-1} (b), $\lambda_{em} = 612$ nm; in LB film deposited at 30 mN m^{-1} (c), $\lambda_{em} = 612$ nm; in LB film deposited at 30 mN m^{-1} (d), $\lambda_{em} = 788$ nm.

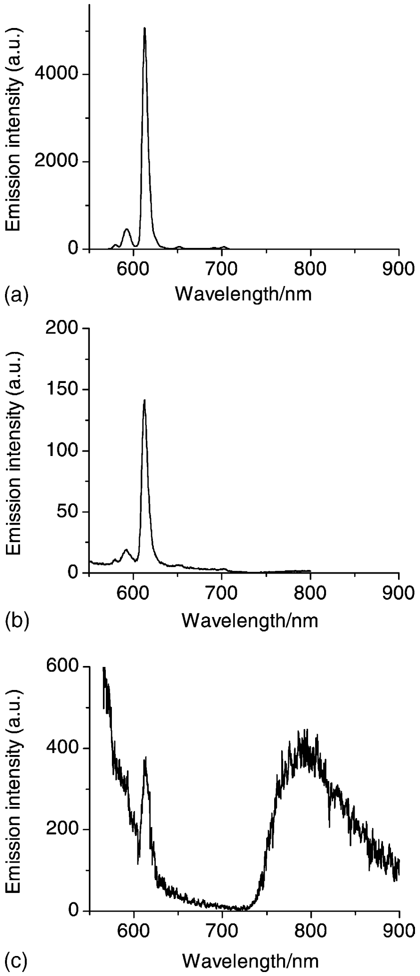

Fig. 4. Emission spectra of Eu(III) complex in compressed powder (a), $\lambda_{ex} = 300$ nm; in LB film deposited at 12 mN m^{-1} (b), $\lambda_{ex} = 326$ nm; in LB film deposited at 30 mN m^{-1} (c), $\lambda_{ex} = 330$ nm.

3.4. Low-angle x-ray diffraction

Low-angle x-ray diffraction patterns for a nine-layer LB film deposited at 30 mN m^{-1} onto optical glass are shown in Fig. 5. Five very sharp Bragg diffraction peaks were found to appear at $2\theta = 2.82°$, $5.68°$, $11.39°$, $14.28°$ and $17.16°$, assignable to (0 0 2), (0 0 4), (0 0 8), (0 0 10) and (0 0 12) Bragg diffractions, respectively. An identity period of 62.6 Å for the Y-type film and single-layer film thickness of 31.3 Å were derived based on following equations:

$$2d_{0\,0\,l} \sin\theta_{0\,0\,l} = \lambda \tag{1}$$

$$D = l d_{0\,0\,l} \tag{2}$$

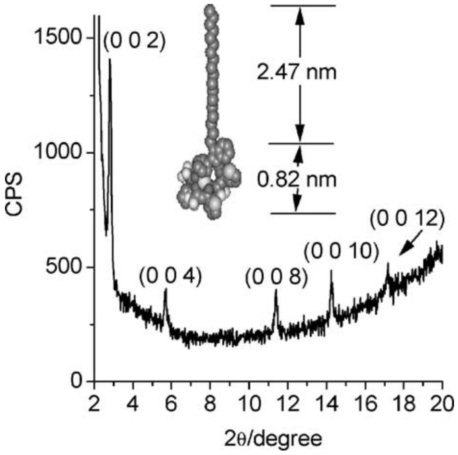

Fig. 5. Low-angle x-ray diffraction patterns of LB film deposited at 30 mN m^{-1} with molecular modeling shown in the inset.

where λ is the wavelength of the incident wave (Cu Kα ray, 0.15418 nm), l the diffraction number, θ_{00l} the incidence angle, d_{00l} the interplane spacing of diffraction index ($00l$), D the identity period of the film. For a Y-type film, thickness of per layer is one-half of D. Theoretical film thickness should be 33.0 Å based on the molecular modeling as shown in the inset of Fig. 5 and assumption that the alkyl chain orientates vertically relative to the substrate surface. The actual tilt angle of the alkyl chain in the film is estimated to be 18° relative to the normal of the substrate surface based on the difference observed between the theoretical film thickness and experimental one. It is noteworthy that the full width at half maximum (fwhm) of the strongest Bragg diffraction peak which is very sensitive to order degree of films, was found to be only 0.16 Å for the LB film in this study, much smaller than the LB films based on metal complexes containing Eu(III) [6c], Pt(II) [9], Ru(II) [12,13], Dy(III) [14], Cu(II) [15], Fe(III) [16], and even a mixed film of a fluorescent Eu(III) complex with stearic acid [7b], indicating highly ordered layered structure of the LB film we prepared.

4. Conclusions

The newly synthesized amphiphilic Eu(III) complex was demonstrated to be of rich surface pressure–area isotherm behaviors and capable of being used for the preparation of the highly ordered LB film based on fluorescent europium(III) complex. UV and emission spectroscopy strongly supported the formation of aggregates in the LB films deposited at high surface pressures, and that the aggregates formed strongly quenched Eu(III) characteristic emission. The efforts are being directed at retaining both highly orderly structure of LB film and strong Eu(III) characteristic emission.

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