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Novel luminescent Langmuir–Blodgett films of europium complex embedded in titania matrix

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Abstract

A stable Eu(DBM)$_3$(DB-bpy)/AA/TiO$_2$ monolayer was formed on the surface of a composite subphase by spreading an Eu(DBM)$_3$(DB-bpy)/AA/TBT chloroform solution. DBM, DB-bpy, AA and TBT refer to dibenzoylmethanate, 4,4′-Di-tert-butyl-2,2′-bipyridine, arachidic acid and tetrabutyloxyltitanium, respectively. Eu(DBM)$_3$(DB-bpy)/AA/TiO$_2$ Langmuir–Blodgett films were deposited on solid substrates and were characterized by low-angle X-ray diffractometry, UV-visible (UV refers to ultra-violet) spectroscopy, photoluminescent spectroscopy and electron probe microanalysis. The results show that a luminescent composite film with layered structure was fabricated, which shows characteristic emission of Eu(III).

PACS: 68.18
Keywords: Langmuir-Blodgett films; Europium complex; Fluorescence; Titania

1. Introduction

Europium complexes have been used as phosphors and laser materials due to their unique luminescent properties [1] arising from the ‘antenna effect’ of the ligands and intramolecular energy transfer from the ligands to central Eu(III) [2–4]. In order to prevent the luminescence of Eu(III) from concentration quenching and to improve thermal and mechanical stability and processing ability, europium complexes have been incorporated into stable matrices for their practical use, such as polymers [5–7], zeolite [8], silica [9–13] and mesoporous materials [14,15].

On the other hand, ordered structures of europium complexes have attracted much attention due to their photophysical properties [16]. Langmuir–Blodgett (LB) technique is a powerful tool to fabricate functional organized films whose components and structure can be designed and controlled exactly [17,18]. The controllable LB films containing europium complexes that may improve the efficiency of the luminescence have been investigated extensively during the last 15 years. Gao et al. found the appropriate conditions for the europium complex monolayer formation [19]. Zhong et al studied the energy migration in the LB films formed by mixed rare earth complexes [20], and Qian et al. studied the photoluminescent properties of LB films of europium complexes and found that the luminescence of the symmetric forbidden transition $^5D_0 \rightarrow {}^7F_0$ of Eu(III) is enhanced in LB films as compared with that in solution [21]. In general, the LB films mentioned above were formed by europium complexes and amphiphilic molecules that were used as matrices.

In addition, Eu(III)/inorganic composite nanoparticles have been investigated widely in recent years [8–15]. It was

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found that the luminescent properties varies with the compositions, and the inorganic matrices can transfer the absorbed energy to Eu(III), similar to the 'antenna effect' of organic ligands. For example, Frendell et al. reported a new sensitized luminescent materials of Eu(III) by TiO_2 nanocrystals [22].

In this paper, organic/inorganic hybrid LB films of $Eu(DBM)_3$(DB-bpy)/AA/TiO_2 (DBM, DB-bpy and AA refer to dibenzoylmethanate, 4,4′-Di-tert-butyl-2,2′-bipyridine, and arachidic acid, respectively) were fabricated and characterized by X-ray diffractometry, transmission electron microscopy, electron probe microanalyzer (EPM), UV-vis and fluorescent spectroscopy.

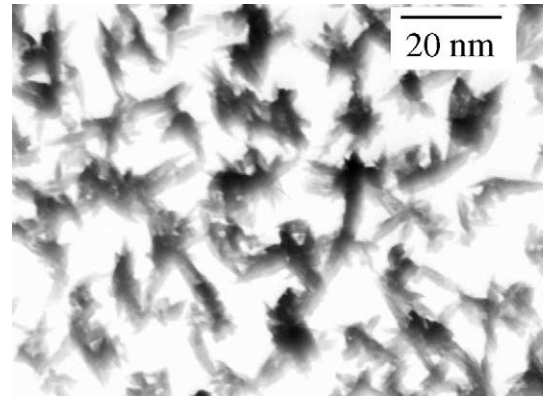


Fig. 1. TEM image of TiO_2 monolayer formed on the surface of the subphase with pH = 12.0 at 20 mN/m.

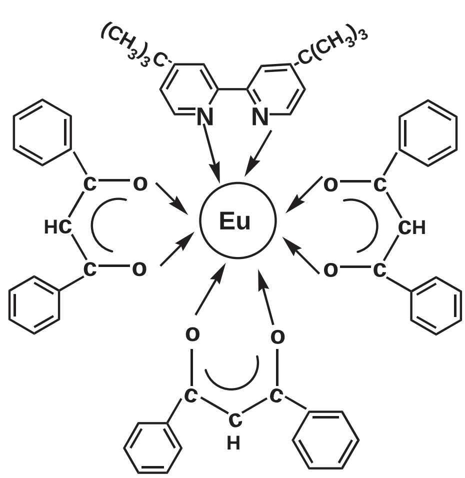
2. Experimental details

2.1. Materials

Eu_2O_3 (99.99%), DBM, DB-bpy and AA were purchased from Aldrich Chem. Co. $Eu(DBM)_3$(DB-bpy) (shown in Scheme 1) was synthesized according to the literature route [23]. Elemental analysis: C: 69.4% (69.4%); H: 5.20% (5.27%); N: 2.56% (2.57%). The values in parentheses are calculated ones. The melting point is 192–193 °C. TBT (tetrabutyloxyltitanium) was obtained from Beijing Agent Plant. Chloroform was dehydrated before being used.

2.2. Method and apparatus

The spreading solution of complex/AA with the molar ratio of 1 : 10 and complex/AA/TBT with the molar ratio of 1 : 10 : 3.3 [24] was prepared by dissolving the corresponding components into the anhydrous chloroform. Pure water and the aqueous solution saturated with the complex and DBM were used as subphase. The pH value of the subphase was adjusted to 12.0 by NaOH aqueous solution.



Scheme 1. Molecular structure of $Eu(DBM)_3$(DB-bpy).

Monolayers were formed by using NIMA 601 Minitrough (Nima Technology, Great Britain) at 20 ± 2°C. The solvent was allowed to evaporate for 30 min prior to compressing. LB films were deposited on a MW-II LB system (Southeast University, China) by vertical dipping method at 20 mN/m with a speed of 10 mm/min. Glass plates and quartz were used as substrates.

Samples for transmission electron microscopy (TEM) (Model JEM-100cxII, Japan) were collected on Formvar-coated, carbon-reinforced 230-mesh copper grids that had been placed in the subphase and positioned at an angle of approximately 15° with respect to the bottom of the container to allow for better drainage before spreading the monolayer by slowly lowering the subphase surface through siphoning the solution out of the container. UV-visible (UV refers to ultra-violet) spectra were recorded with a HP 8453E diode array spectrophotometer (Hewlett-Packard Co., USA) in the range 190–820 nm, with a resolution of 2 nm. Excitation spectra and emission spectra of the composite films were recorded by using a FLS920 fluorescence spectrophotometer (ENDINBURGH, U.S.A). The LB films were investigated by an electron probe microanalyzer (JXA-8800R, Japan). X-ray diffraction patterns were obtained by using a D/Max-γB X-ray

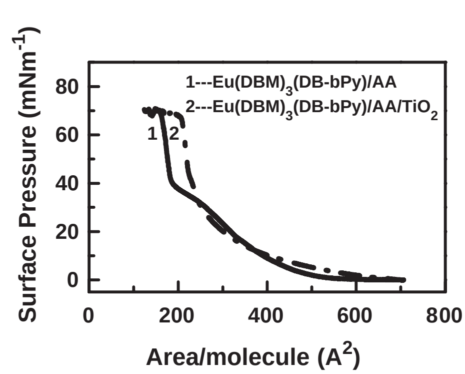


Fig. 2. π-A isotherms of $Eu(DBM)_3$(DB-bpy)/AA and $Eu(DBM)_3$(DB-bpy)/AA/TiO_2 monolayers on the composite subphase surface.