

## 稀土 Eu(Ⅲ)双酞菁衍生物 LB 膜的荧光性

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合成了八-4-(四氢糠氧基)酞菁钕(Ⅲ), 通过元素分析、红外光谱、质谱和紫外-可见光谱加以确认。测定了配合物的  $\pi$ -A 曲线, 证明它有有的成膜性 Z 型沉积形成的 LB 膜材料有很强的荧光响应, 随着 LB 膜厚度的增加, 荧光性增强。掺杂邻菲咯啉形成的混合 LB 膜, 其荧光性比纯膜强。但不是邻菲咯啉加入的量越多荧光性越强。配合物: 邻菲咯啉 = 1: 10 时 (摩尔比), 有最好的荧光行为。用电子光谱对 LB 膜的结构进行了表征。

关键词: 稀土双酞菁 邻菲咯啉 LB 膜 荧光性 合成 掺杂  
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## Luminescent Properties of Langmuir-Blodgett Films of Europium Bisphthalocyanine

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Eu(Ⅲ)-octa-4-(tetrahydrofurfuroxy) phthalocyanine ( $\text{EuPc}_2'$ ) was synthesised and characterized by elementary analysis, IR, MS, UV-vis spectra.  $\text{EuPc}_2'$  has good film-forming ability from determination of isotherm of  $\pi$ -A. The complex LB film was formed by depositing of  $\text{EuPc}_2'$  on a quartz slide with the LB techniques of the Z-type. The luminescent properties of pure and doped LB films were determined. The results showed that pure films have good luminescent properties, the thicker the LB films, the stronger the fluorescent intensity. The films doped with o-phenanthroline (abbreviated as phen) made the relative intensity of fluorescent emission behavior enhance in comparison to that of pure LB film. But the amount of phen may be not too much. Our results showed that  $\text{EuPc}_2'$ : phen = 1: 10 (molar ratio) has the best fluorescent behavior. The electronic spectroscopic characterization of the LB films is also given.

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## 0 Introduction

The fluorescence of aromatic hydrocarbons can activate tertiary amines. The photoinduction is accompanied with the appearance of a broad structureless band to the red of the fluorescence of the hydrocarbon monomer in non-polar solvents. This new emission band is associated with the complex formed between the excited hydrocarbon  $A^*$  and the electron donor amine D, and is called an exciplex. With the incorporation of two, three or more chromophores into a single molecule separated by non-conjugated bonds, an intramolecular exciplex forms readily<sup>[1]</sup>. The quenching of 9-methylanthracene fluorescence by piperazines and the formation and decay of intermolecular exciplexes can be determined together with the rate constants using the single-photon-counting technique<sup>[2]</sup>. The results showed that the formed exciplex involved only one. Amino group, while the second amino group in the piperazine ring can deactivate the exciplex via other radiative and non-radiative processes. Studies of the interactions between an electron donor and an electron acceptor in an intramolecular exciplex may gain an insight into the mechanism of photoinduced electron transfer and primary charge separation in complex biological redox systems such as those involved in photosynthesis.

Phthalocyanine structure is similar to haemoglobin. The studying on fluorescence of rare earth bisphthalocyanine for understanding the organic system and repeat organic characteristics is greatly active<sup>[3]</sup>. Phen as the cooperating reagents, intersystem crossing through charge transfer to produce a localized triplet state is an important pathway of activation of rare earth bisphthalocyanine.

Langmuir-Blodgett (LB) film-forming technique is a highly attractive method for producing well-ordered and thickness-controllable organic thin films. Phthalocyanine and metallophthalocyanine are well known for their thermal and chemical stability to produce LB films. The use of phthalocyanine and deposition technique show a great potential for improving the performance of fluorescence.

In this paper, preparation, characterization and determining electrical properties and fluorescent emission behavior of the Eu (III) -octa-4-(tetrahydrofurfuroxy) phthalocyanine ( $\text{EuPc}_2'$ ) (Fig. 1) LB film are reported.

## 1 Experimental

### 1.1 Synthesis

The synthesis of 4-(tetrahydrofurfuroxy)-1, 2-dicyanobenzene: 2.5g (14.45mmol) of 4-nitro-1, 2-dicyanobenzene, 2.0g (19.60 mmol) of tetrahydrofurfuryl alcohol in 25 mL of DMSO were placed into reactor, and then 3.0 g of  $\text{K}_2\text{CO}_3$  was added in it. The mixture was stirred at 45 ~ 50°C for 24

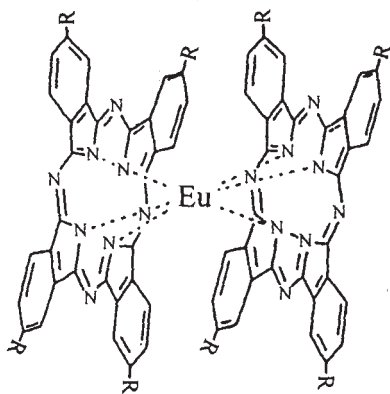


Fig. 1 Molecular structure of europium bisphthalocyanine

h under  $N_2$  atmosphere. After cooling to room temperature, it was poured into ice-water with stirring. The precipitate was filtered out and washed by distilled water. After drying it was recrystallized in  $CH_3OH$  to give 1.9g in the yield of 43.8% with m. p.  $90 \sim 91^\circ C$ .

Eu(III)-octa-4-(tetrahydrofurfuroxy) phthalocyanine ( $EuC_{104}H_{97}O_{16}N_{16}$ ) was prepared by the reaction of 1.5g(0.759 mmol) of 4-(tetrahydrofurfuroxy)-1,2-dicyanobenzene with Europium acetate of 0.25g(0.820 mmol) in an evacuated glass ampoule at  $24^\circ C$  for 24h. The crude products were milled, dissolved in chloroform and separated through a chromatographic column (aluminum oxide of 100 mesh). The green solution was obtained to give 2.1g in the yield of 67.2%. Elemental analysis (calc.) C: 64.18(63.11) H: 4.62(4.05) N: 11.89(11.33) Eu: 7.65(7.68). MS/(m/e): 1975 IR (KBr pellet  $cm^{-1}$ ): 747 w(ring deformation), 891 w, 1089 w (Pc ring), 1228.6 s( $\nu_{pc-o}$ ), 1316.5 w(pyrrole stretch), 1479.8 vs( $\nu_{pc-C=N}$ ), 1528 w( $\nu_{pc-C=N}$ ), 1608 m( $\nu_{pc-C=C}$ , benzene stretch), 2806 m( $\nu_{-CH_2-}$ ), 1251 s( $\nu_{-OR_2-}$ ) [4].

## 1.2 Film deposition

Complex  $EuPc_2'$  were dissolved in the chloroform solution with  $0.1mg \cdot mL^{-1}$ . The phen were mixed in the solution of  $EuPc_2'$  according to the different molar ratio. The quartz substrates have been cleaned by Soxhlet in isopropyl alcohol for 10 hours, then by ultrasonic treatment for ten minutes in chloroform, methanol and pure water respectively. The fabrication of LB films was carried out on KSV-5000 (KSV, Fenland) twin-troughs LB instrument. The  $EuPc_2'$  solution was spread onto pure water. After chloroform was evaporated, the  $EuPc_2'$  monolayer was compressed using a constant surface pressure of  $20mN \cdot m^{-1}$  and then transferred onto the substrate by Z-type dipping at the speed of  $5mm \cdot min^{-1}$  (Fig. 2) (yield deposition ratios of unity). A number of  $EuPc_2'$  LB film with different thickness and various ratio of phen were made. Fluorescent behavior were measured on a SPEXFL<sub>2</sub>T<sub>2</sub> spectrometer (U.S), and the narrow length was 2 mm.

## 1.3 Spectrum analysis

The structure of the LB films must be characterized. The polarization plane or incident beam was chosen perpendicular to the dipping direction and the glancing angle selected exper-

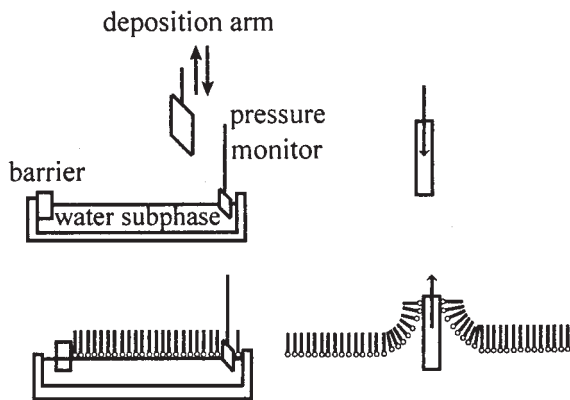


Fig. 2 LB film deposition Z-type

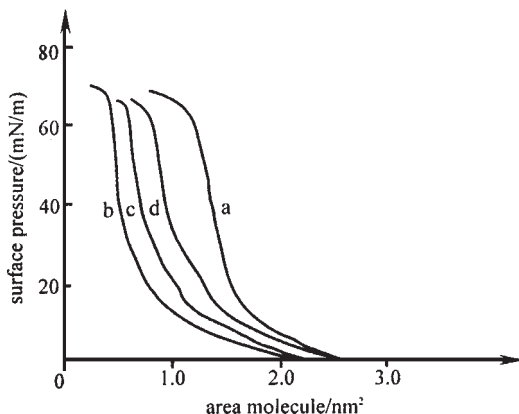


Fig. 3  $\pi$ -A isotherm of  $EuPc_2'$  and Phen  
a:  $EuPc_2'$ , b: Phen, c:  $EuPc_2'$ : Phen = 1:5,  
d:  $EuPc_2'$ : Phen = 1:10

imentally was  $0^\circ$  and  $30^\circ$ . The variation of optical absorbance in the visible region was monitored using UV-vis spectrometry.

## 2 Results and discussion

### 2.1 Isotherm

The isotherm of Eu bisphthalocyanine given in Fig. 3a possess the distinctive 'three-phase' structure characteristics. The isotherm is retained on recompression. The collapsing pressure of the monolayer is  $70\text{mN} \cdot \text{m}^{-1}$ . The area per molecule ( $1.8\text{nm}^2$ ) is obtained by extrapolating the steeply rising part of the curve to zero pressure.

The isotherms of phen and EuPc<sub>2</sub>'/phen mixture were shown in Fig. 3b, c, d respectively. With the increasing of phen content the collapsing pressure of the monolayer are constant ( $70\text{mN} \cdot \text{m}^{-1}$ ) but the area per molecule is decreasing. It means that the doped phen does not effect good film-forming ability of complex.

### 2.2 Orientation of EuPc<sub>2</sub>' molecules

In order to evaluate the particular orientation EuPc<sub>2</sub>' molecules on LB films, Cartesian Coordinates ( $X$ ,  $Y$ ,  $Z$ ) are introduced as shown in Fig. 4a. The  $Y$ - and  $Z$ -axis are chosen to be parallel to the dipping direction and normal to the substrate respectively. To simplify the situation, the phthalocyanine ring is considered as a flat circular plate which the  $\pi$ - $\pi^*$  transitions dipole is uniformly distributed. The center axis of the plate,  $Z'$ , is oriented at an angle  $\theta$  to the  $Z$ -axis with an azimuth of  $\Phi$  in the  $X$ - $Y$  plane. When polarized light is illuminated on the film at angle  $\beta'$  to the  $Z$ -axis in the  $Z$ - $X$  plane with a refraction angle  $\beta$  inside the layer (Fig. 4b), the dichroic ratio  $D_\beta = A_{//} / A_\perp$  ( $A_{//}$  and  $A_\perp$  are the absorbance of film for polarized light with electric vectors parallel ( $//$ ) and perpendicular ( $\perp$ ) to the dipping direction, respectively, can be expressed as.

$$D_\beta = [\langle \cos^2 \varphi \rangle + \langle \cos^2 \theta \sin^2 \Phi \rangle] / [\langle \sin^2 \Phi \rangle + \langle \cos^2 \theta \cos^2 \varphi \rangle] \cdot \cos^2 \beta + \langle \sin^2 \theta \rangle \sin^2 \beta \quad (1)$$

where  $\langle \rangle$  denotes a statistical average.

Thus, the orientation of the  $Z$ -axis can be estimated by simply investigating the dependence of  $D_\beta$  on  $\beta$ . One of the easiest ways would be to measure  $D_\beta$  at two different angles,  $\beta = 0^\circ$  and  $\beta = 30^\circ$ , and to calculate  $\langle \cos^2 \theta \rangle$  and  $\langle \sin^2 \theta \cos^2 \varphi \rangle$  by the following equations:

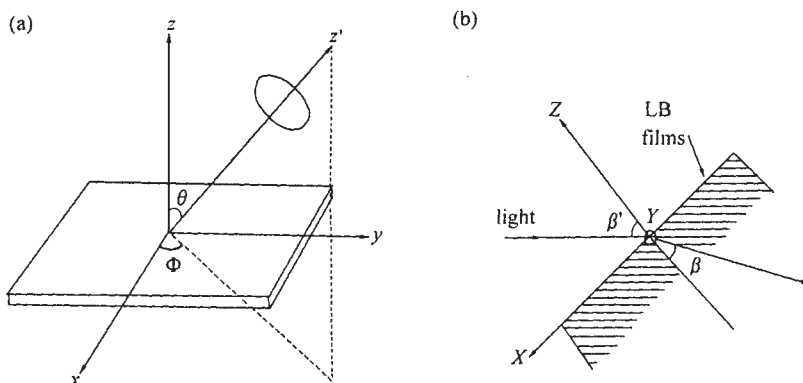


Fig. 4 (a) Coordinates ( $x$ ,  $y$ ,  $z$ ) for expressing Eu bisphthalocyanine orientation  $y$ -axis: dipping direction;  $z$ -axis: center axis of Eu bisphthalocyanine represented by the circular plate; (b) Direction of polarized incident light on the substrate

$$\langle \cos^2\theta \rangle = \frac{D_0 - (1 + D_0 \sin^2\beta) D_{30}}{(1 - 2\sin^2\beta) D_{30} - (1 + D_{30} \sin^2\beta) D_0} \tag{2}$$

$$\sin^2\theta \cos^2\Phi = \frac{D_0 - \langle \cos^2\theta \rangle}{1 + D_0} \tag{3}$$

$$D_\beta = A_{//} / A_{\perp} \tag{4}$$

Using a dichroic ratio at 690 nm,  $D_0 = 0.82$  and  $D_{30} = 0.29$ , the orientation angles could be calculated as  $\theta = 35.7^\circ$  and  $\varphi = 57.5^\circ$ .

2.2 Spectroscopic characterization

The absorption spectrum for a ten-layer EuPc'2 LB films is illustrated in Fig. 5. The Q-band split into two maximum peaks at 690 and 719nm. Also shoulder peak splits into 620 and 660nm, respectively. The spectrum is typical in the spectra of solid lanthanide bisphthalocyanine derivatives<sup>[5]</sup>.

The peaks of pure and doped film were greatly similar, but the  $\lambda_{max}$  of doped film was slight red-shift about 7nm and attributed to that phen took part in the conjugation with phthalocyanine. It can be deduced from the following

Transannular effect and position resistance that may take place easier among molecules in doped film. These effects lead to energy decreased in symbol  $\pi-\pi^*$  transition between ground and excited state energy level. So the absorption band is shifted to red direction. It indicated further that doped phen in the film made the fluorescent intensity increase, i.e the larger conjugated-system, the stronger fluorescent behavior<sup>[6]</sup>.

2.3 Fluorescent behavior of compound films

The fluorescent behavior of pure LB films was related to the thickness of LB films. Table. 1 demonstrates that the thicker the EuPc2' LB film, the stronger the relative fluorescent intensity. In Table 1 with same excited wavelength for 375nm, the relative intensity is following the order (layer)  $40 > 30 > 20 > 10$ .

Table 1 Fluorescent Emission Behavior of Different Layers of LB Films

layer	emission	relative strength	
	wavelength/nm	$1 \times 10^2$	assignment
40	592	1150	$^5D_0 \rightarrow ^7F_1$
	620	2030	$^5D_0 \rightarrow ^7F_2$
30	594	750	$^5D_0 \rightarrow ^7F_1$
	622	1460	$^5D_0 \rightarrow ^7F_2$
20	591	500	$^5D_0 \rightarrow ^7F_1$
	623	900	$^5D_0 \rightarrow ^7F_2$
10	596	480	$^5D_0 \rightarrow ^7F_1$
	622	800	$^5D_0 \rightarrow ^7F_2$

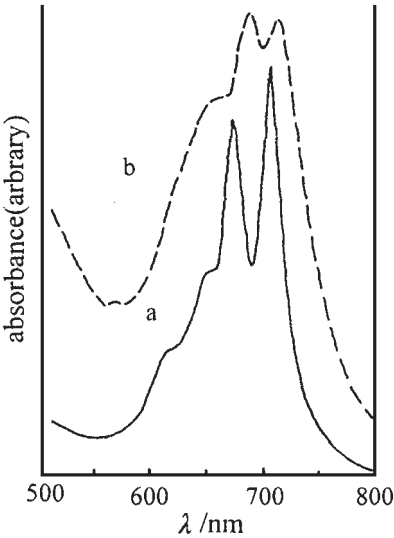


Fig. 5 UV-vis spectrum of 10-layer films  
a: pure b: doped

The doped LB films with 40 , 30, 20 layer were formed by the complex  $\text{EuPc}_2'$  and phen according to  $\text{EuPc}_2': \text{phen} = 1: 10$  (molar ratio) and then compared with the pure LB film of 40 layers . When the fluorescent excitation is at 375 nm, the relative intensity of emission behavior with doped LB films (Table 2) is stronger than that of the pure film with the same layers , as a matter of fact the doped LB film with 30 layer is also stronger than it. It means that phen has been doped into LB film and plays an important role in transmitting intermolecular energy as the cooperating reagents so that the relative fluorescent intensity with the doped LB films was much strong . However the large amount of doped phen are unfavorable. For example for molar ratio  $\text{EuPc}_2': \text{phen} = 1: 20$  and  $1: 30$  (20 layer) the relative intensity (Table 3) was decreasing according to the order (molar ratio)  $10 > 20 > 30$ .

**Table 2 Fluorescent Emission Behavior of the Pure and Doped LB Films of Constant A: phen = 1: 10 Emission**

LB films	emission	relative strength	assignment
layer	wavelength /nm	$1 \times 10^3$	
doped	598	1100	$^5D_0 \rightarrow ^7F_1$
40	623	3200	$^5D_0 \rightarrow ^7F_2$
doped	597	1000	$^5D_0 \rightarrow ^7F_1$
30	622	2002	$^5D_0 \rightarrow ^7F_2$
pure	599	450	$^5D_0 \rightarrow ^7F_1$
40	624	1100	$^5D_0 \rightarrow ^7F_2$
doped	598	500	$^5D_0 \rightarrow ^7F_1$
10	624	850	$^5D_0 \rightarrow ^7F_2$

**Table 3 Fluorescent Emission Behavior of the Pure and Doped LB Films of Different Ratio with A: phen**

molar ratio	emission	relative	assignment
	wavelength /nm	strength $1 \times 10^2$	
1 : 10	595	650	$^5D_0 \rightarrow ^7F_1$
	620	1750	$^5D_0 \rightarrow ^7F_2$
1: 20	595	600	$^5D_0 \rightarrow ^7F_1$
	620	1100	$^5D_0 \rightarrow ^7F_2$
1: 30	593	505	$^5D_0 \rightarrow ^7F_1$
	618	1050	$^5D_0 \rightarrow ^7F_2$
pure	593	450	$^5D_0 \rightarrow ^7F_1$
	620	850	$^5D_0 \rightarrow ^7F_2$

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