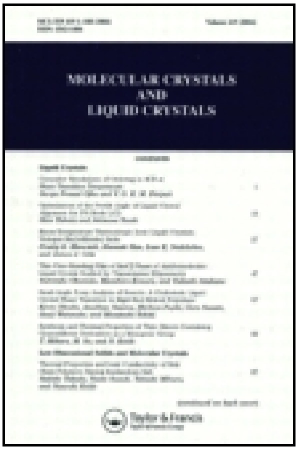

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Light Emitting Langmuir-Blodgett Films

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ABSTRACT Langmuir-Blodgett films of europium tri-behenate, behenamido benzoate, 2-(4'-dodecylbenzoyl)benzoate-palmitate (1:1) mixture (EDBB/P) and 2-(4'-eicosoxy benzoyl)benzoate-arachidate (1:1) mixture were prepared and their UV absorption and photoluminescent properties were compared with solutions. Fluorescence intensities of LB films of EDBB/P were greatly enhanced by both effects of the large absorption of excitation light and the efficient energy transfer from organic molecules to Eu^{3+} ion. This enhancement is due to the preferable molecular alignment of LB films.

INTRODUCTION

Although most of organic dyes show strong absorption bands in UV-visible spectral region, excited electrons return to the initial ground states without emitting any light. On the other hand, lanthanide metal ions display photoluminescence when their electrons are excited, though their quantum efficiencies are rather small. Interestingly, if we could hybridize organic dyes with lanthanide metal ions, then the photoluminescence intensity would be significantly enhanced, in which the energy generated by the photoexcitation of a dye would be transferred to the lanthanide metal ion(1,2). Furthermore, if we could introduce noncentrosymmetry in the molecular assemblies and fabricate a cavity with a mirror or a grating mirror at both edges of a device, the luminescent light will be amplified in the cavity to permit laser light. This hybridization of organic dyes with lanthanide metal ions offers multifunctional new devices.

Langmuir-Blodgett film technique is one of the most suitable method to hybridize organic dyes with luminous ionic materials. A monolayer can be formed from amphiphilic molecules possessing a light absorption site by including metal ions into the subphase. Luminous ultrathin films capable for dissipating heat can be prepared by using lanthanide metal. In this report, the luminescent characteristics of europium LB films will be discussed.

EXPERIMENTAL

Behenamidobenzoic acid (BABA) and 2-(4'-dodecylbenzoyl)benzoic acid (DBBA) were synthesized according to the scheme shown in Figs.1 and 2, respectively. The former was prepared from behenoyl chloride and 4-aminobenzoic acid methyl ester. Dodecanoylbenzene of the latter was prepared by the Friedel-Crafts reaction of benzene and dodecanoyl chloride in the presence of anhydrous $AlCl_3$. Then it was reduced to dodecylbenzene by the Wolff-Kishner reaction. DBBA was prepared by the Friedel-Crafts reaction with phthalic anhydride.

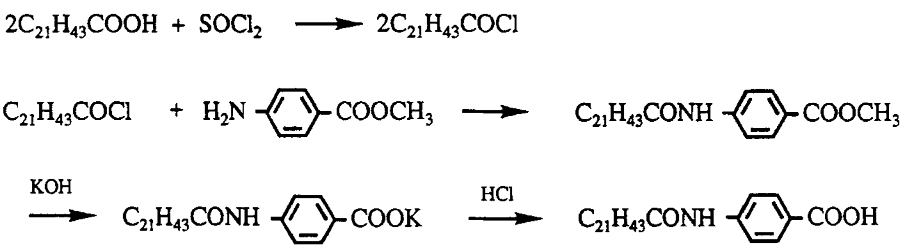

Fig. 1 Synthesis of behenamidobenzoic acid

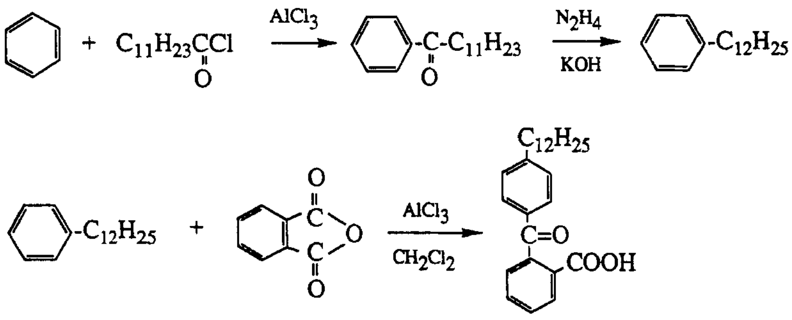

Fig. 2 Synthesis of 2-(4'-dodecyl benzoyl) benzoic acid

A lanthanide metal ion, Eu^{3+}, was used in order to get fluorescence spectrum that lie in the range of the spectrophotometer. The UV absorption and luminescent properties of $EuCl_3$ were measured in distilled water. Those of BABA, stearylaminophenylacetic acid (SAPAA), Eu^{3+} tri-behenamidobenzoate (EBAB), and

Eu^{3+} tri-stearylaminophenyl acetate (ESAPA) were measured in N,N-dimethyl formamide (DMF) and ethanol (1 : 9 volume ratio) mixed solutions. Those of Eu^{3+} tri-(2-(4'-dodecylbenzoyl)benzoate) (EDBB) and Eu^{3+} tri-(2-(4'-eicosoxybenzoyl) benzoate) (EEBB) were also measured in N,N-dimethylacetamide (DMA) and benzene (1:1) mixed solutions. Model Ubest-30 UV/VIS spectrophotometer of Japan Spectroscopic Co., LTD and Hitachi Model F-3000 fluorescence spectrophotometer were used to measure ultraviolet and fluorescence spectra.

20 layers of EBAB and Eu^{3+} tri-behenate (EB) were deposited onto quartz plates. Since EDBB and EEBB had difficulties to be transfered onto the substrates even though they formed good monolayers, therefore, LB films were prepared from 1:1 mol mixture with palmitic acid (EDBB/P) and arachidic acid (EEBB/A) respectively, by using a Nippon Laser Electronics LB trough. This trough has moving wall and can transfer even a stiff monolayer containing trivalent ions to a substrate(3). Their fluorescence intensities were measured by 30 to 45 degrees incident light angle to the quartz substrate.

RESULTS AND DISCUSSION

Fig.3 shows UV absorption spectra of $EuCl_3$, BABA, and SAPAA in the solutions. BABA has UV absorption band at 270 nm and its ε is 1.8×10^4. $EuCl_3$ has some small absorption bands at 392, 316, and 297 nm, and its ε at 392 nm is only 1.8. Absorbance was 10^4 times larger in BABA solution than that of $EuCl_3$ solution. Consequently, it can be said that the UV light was significantly absorbed by BABA. The fluorescence of Europium salt of BABA (EBAB) solution is much stronger than that of $EuCl_3$ itself. These results suggest that the energy generated by the photoexcitation of organic molecule was transferred to Eu^{3+} ion.

The UV absorption spectrum of SAPAA in the solution showed a peak at lower wavelength than that of BABA and its absorbance of $\varepsilon = 1.3 \times 10^4$ was smaller than BABA. But the fluorescence intensity of ESAPA dropped more drastically compared with those of EBAB. This means the introduction of methylene group blocks the energy transfer from phenyl rings to Eu^{3+} ion.

The π-A curves of EEBB, Eu^{3+} tri-arachidate (EA), and EEBB/A are shown in Fig.4. Since EEBB showed typical π-A behavior of expanded films and could not be transfered to a substrate, 1 : 1 mixture of EEBB and arachidic acid were prepared. The π-A curve of the mixture shows two condensed phases at around 25 and 10A. It is usually said that the film prepared at low pressure is a mixed film of two components and a multilayer is formed at high pressure(4). Therefore the LB films of EEBB/A was prepared at the first condensed phase in which the surface pressure was 18 mN/m.

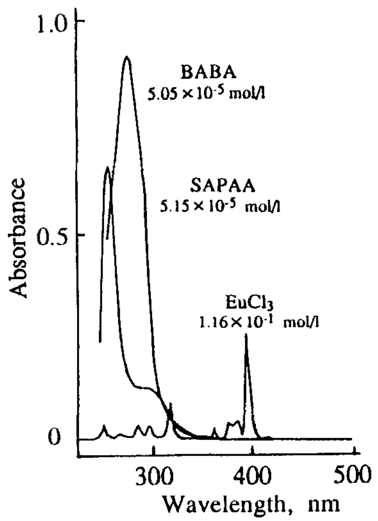

Fig. 3 UV absorption spectra of behenamidobenzoic acid (BABA) and stearylaminophenylacetic acid (SAPAA) in DMF/ethanol and EuCl$_3$ in water.

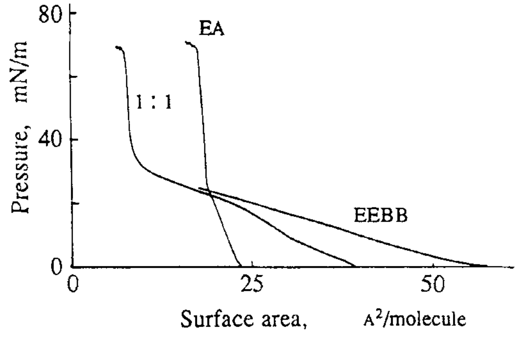

Fig. 4 π-A curves of Eu^{3+} tri-(2-(4'-eicosoxybenzoyl)benzoate) (EEBB), arachidate (EA), and their mixture (1:1).

The fluorescence intensity of EBAB LB films was much stronger than that of EB. This remarkable difference can be explained by the difference of chemical structures. The result shows that EBAB has a larger absorption of excitation light in the molecule. On the other hand, EB doesn't absorb the incident light because the molecule consists mainly of alkyl chain. Therefore molecules with large absorption coefficient must be designed. Fig. 5 shows the fluorescence spectra of EDBB/P. Though only two or three layers are deposited on the substrate, the highly efficient fluorescence was observed with naked eye. The fluorescence intensities of LB films of EBAB and EDBB/P were compared with their solutions. The calculated intensity per Eu^{3+} ion was 4 and 100 times larger for EBAB and EDBB/P LB films respectively than their solutions. These results indicate that the highly efficient fluorescence occurs due to the preferable molecular alignment, which was formed by the LB-technique capable to be excited by the incident light.

In comparison with the excitation spectra of EDBB and EEBB in the solution, EEBB has a broader peak than EDBB at the same wavelength region, so that it shows 4 times stronger fluorescence intensity. EEBB/A , in which a longer alkyl chain is introduced, could be prepared as more stable LB films than EDBB/P. X-ray diffraction pattern of the films showed clear peaks up to (005) reflection and a layer spacing of 28.4 A was calculated from the pattern. The fluorescence intensity of EEBB/A LB films was 1/10 weaker than that of EDBB/P beside the fact that it showed stronger fluorescence intensity in the solution. We assume that this difference can be explained by the difference of molecular alignment in LB films. The further detailes will be reported in near future.

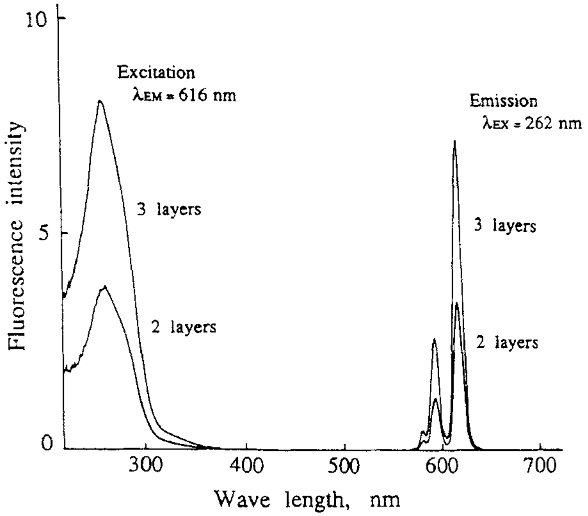

Fig. 5 Fluorescence spectra of LB films of Eu^{3+} tri-(2-(4'-dodecylbenzoyl)benzoate) and palmitate mixture.

CONCLUSIONS

From this study, the following conclusions can be drawn;

1. The fluorescence intensities of LB films were greatly enhanced by both effects of the large absorption of excitation light and the efficient energy transfer from organic molecules to a Eu^{3+} ion. This enhancement is due to the preferable molecular alignment in a LB film, enable to absorb the incident light.

2. Although the UV absorption of SAPAA peak decreased only 72% to that of BABA, the fluorescence and excitation intensity of ESAPA dropped drastically compared with those of EBAB. This means the introduction of methylene group blocks the energy transfer from phenyl rings to a europium trivalent ion.

3. Although more stable LB films could be prepared by introducing a longer alkyl chain to EDBB, but the fluorescence intensity decreased. It is assumed to be due to the difference of molecular alignment in a LB film.

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