Enhanced Luminescence of Eu(III) by La(III), Gd(III), Tb(III) and Y(III) in Langmuir-Blodgett Films of Mixed Rare Earth Complexes

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Four kinds of LB films containing 0.5%Eu(TTA)3Phen + 99.5%RE(TTA)3Phen (in molar percentage; RE = La(III), Gd(III),Tb(III) and Y(III)) mixed with arachidic acid (AA) in molar ratio of 1:1 were fabricated. The luminescent enhancement effect of RE(TTA)3Phen on Eu(III) was studied. The influence of rare earth ions on the efficiency of the intermolecular energy transfer in films was discussed. When the complexes of Tb(III) and Gd(III) coexist with Eu(TTA)3Phen, the efficiency of energy transfer is higher than that of the complexes of La(III) and Y(III).

The Langmuir-Blodgett (LB) technique has been used for fabricating functional organized films because of its properties of controlling molecular arrangement effectively and designing compositions and structures artificially.[1] Recently LB films of europium(III) complexes with β-diketone ligands have been reported and their optical characteristics have been studied.[2-4] But little work focused attention on the luminescent enhancement effect of rare earth complexes in LB films.[5] In this work, LB films of rare earth complexes 0.5%Eu(TTA)3Phen + 99.5%RE(TTA)3Phen (TTA = thenoyltrifluoroacetone, Phen = 1,10-phenanthroline) mixed with AA were made by the LB technique. The luminescent enhancement effect of the complexes of La(III),Gd(III),Tb(III) and Y(III) on Eu(III) in the films was studied and the influence of these rare earth ions was discussed.

Rare earth oxides were obtained in purities of 99.9% or better. The complexes studied here were synthesized according to the literature 6. The target complexes with good purities were produced.[7]

With reference to conditions that the enhanced luminescence existed in micellar systems,[8,9] the magnitude of 0.5% Eu(TTA)3Phen in film-forming materials was chosen. The compositions of LB films studied here are as follows:

LB1 (0.5%Eu(TTA)3Phen+99.5%La(TTA)3Phen):AA=1:1
LB2 (0.5%Eu(TTA)3Phen+99.5%Gd(TTA)3Phen):AA=1:1
LB3 (0.5%Eu(TTA)3Phen+99.5%Tb(TTA)3Phen):AA=1:1
LB4 (0.5%Eu(TTA)3Phen+99.5%Y(TTA)3Phen):AA=1:1
LB5 (0.5%Eu(TTA)3Phen+99.5%AA):AA=1:1

The film-forming materials mixed with AA in molar ratio of 1:1 were dissolved in chloroform with given concentrations. The aqueous subphases were saturated with the film-forming materials, TTA and Phen to inhibit dissolution and dissociation of the complexes in water.[5]

A British NIMA 2000 round trough was used for drawing the surface pressure-area (π-A) isotherms and depositing the LB films. Hydrophobic optical glass substrates were used for deposition LB films in Y-type model with the speed of 10 mm min^{-1}. Transfer ratios were around unity. Figure 1 shows the π-A isotherms at the temperature of 20± 2°C. The numbers marking curves are corresponding to LB1-LB5, respectively. Long platforms in the curves of 1-4 indicate the process of a phase change. In the case of containing La(TTA)3Phen a low platform is observed. Because complex of Eu(TTA)3Phen is minute quantity, the isotherms in Figure 1 show the properties of RE(TTA)3Phen and AA practically. From the isotherms a surface pressure of 20 mNm^{-1} was chosen for depositing these films to secure the certain concentration of Eu(TTA)3Phen in the films. At this pressure, the average area of 65 $Å^2$ per molecule for complex can be calculated.

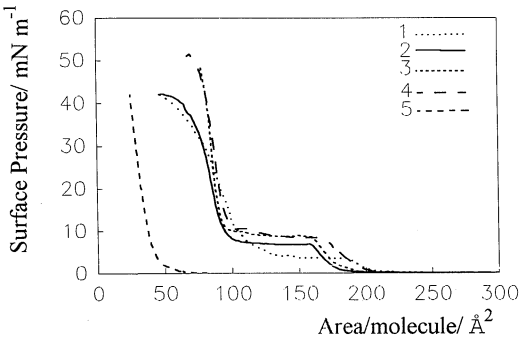

Figure 1. π-A isotherms of LB1-LB5 at the compressing rate of 20 cm^2/min.

The fluorescence intensities of LB films were determined on a Hitachi 850 fluorescence spectrophotometer. The fluorescent excitation and emission spectra of 10-layer LB2 are shown in Figure 2. At the excitation wavelength of 350nm, the strongest emission peaks to LB1-LB4 were observed at 612nm. This peak was used for the following measurements. Figure 3 shows the relation between the fluorescence intensities and the number of layers. The linear relation indicates that the films were transferred successfully. Figure 4 is a low angle X-ray diffractrogram (LAXRD) for 20-layer films of LB2. It shows that the films have a periodic structure. From LAXRD, an average layer spacing 49.6 Å was obtained. Therefore, the film thickness of 24.8 Å was derived based on the Y-type films. It means that the molecules of AA determine the distance of every layer in the films. According to the results of this work, a possible arrangement of molecules in LB films is illustrated in Figure 5.

To prove the luminescent enhancement effect and compare the efficiency of different rare earth ions, the molecules of RE(TTA)3Phen were substituted by those of AA. Consequently, the films LB5 were fabricated. The efficiency of enhanced luminescence was obtain by comparing the fluorescence intensities of 10-layer films LB1-LB4 with that of LB5, respectively. The results are listed in Table 1. They reveal that the luminescent enhancement effect exists in the films clearly.

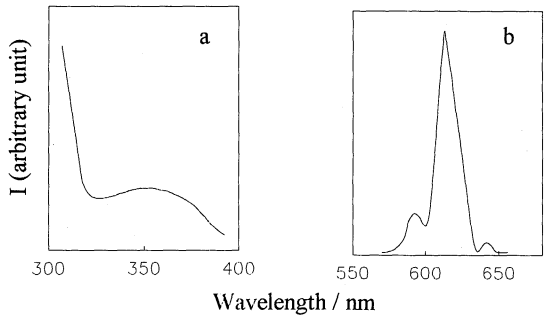

Figure 2. Excitation and emission spectra of 10-layer LB2.
a --- excitation b --- emission

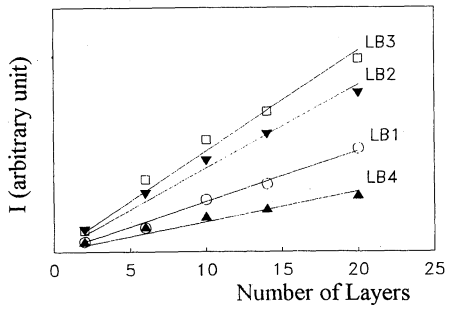

Figure 3. The relation between emission intensity and the number of layers for LB1-LB4.

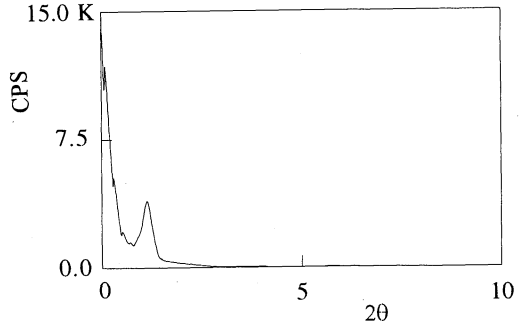

Figure 4. Low angle X-ray diffractrogram for twenty-layer films of LB2.

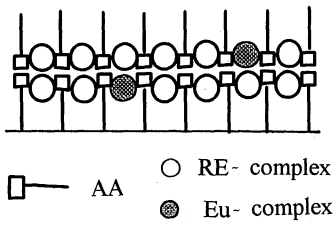

Figure 5. A possible structure for LB films.

Table 1. The luminescent enhancement efficiency of LB1-LB4

LB	1	2	3	4
Efficiency [10]	65	125	145	40

This phenomenon was used for determination of trace amounts of europium in analytical chemistry when a surfactant was added to the solution and micelle were formed.[8,9] In the condition of micellar system, the distance among molecules is very close. An intermolecular energy transfer may be performed effectively from RE(TTA)3Phen to Eu(TTA)3Phen. In LB films, the organized arrangement of molecules allows the intermolecular energy transfer to perform more effectively. The efficiency of energy transfer is not only concerned with the triplet level of ligand TTA,[11] but also dependent on the central ions by the results of this work. Following order is obtained: Tb(III), Gd(III) >> La(III), Y(III). It is also obtained in the system of (0.5% Sm(TTA)3Phen + 99.5% RE(TTA)3Phen):AA=1:1[12]. These indicate that the closer the radii of RE(III) to Eu(III) are, the higher efficiency of energy transfer is obtained. This result corresponds to that obtained in the micellar system.[13] Therefore, LB films would be a suitable system for studying the triplet energy transfer.

In conclusion, we have seen that the fluorescence intensity of Eu(III) is enhanced obviously when the complexes of RE(TTA)3Phen coexist in the LB films. The higher efficiency of energy transfer may be observed when the complexes of Tb(III) and Gd(III) are substituted for those of La(III) and Y(III). This effect may be used for making luminescent devices and will have an advantage for reducing the price of materials. The further research is on going.

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References and Notes

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