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Energy Transfer Between Europium Complexes and a Porphyrin Derivative in Monolayer Assemblies

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ENERGY TRANSFER BETWEEN EUROPIUM COMPLEXES AND A PORPHYRIN DERIVATIVE IN MONOLAYER ASSEMBLIES

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Abstract Monolayers of europium complexes and a porphyrin derivative (TSPP) were investigated and their LB films were transferred onto hydrophobic substrates with given patterns. The emission from Eu complexes is quenched to about 30% of the original intensity when they are alternatively deposited by one layer of TSPP, suggesting an energy transfer from Eu complexes to TSPP. The critical transfer distance for Eu complexes and TSPP is about 75 Å.

INTRODUCTION

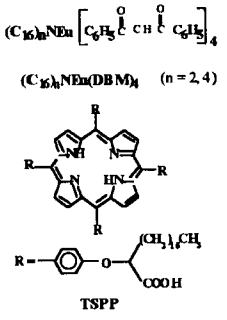
The photophysical properties for luminescent compounds in Langmuir-Blodgett films have been widely investigated.[1,2] It is considered that light conversion between metal complexes or energy donors and acceptors is a valuable way for the development of the optical devices, studies on biochemistry, and so on.[3] Since Waissman found that europium β-diketonate complexes give off strong emissions under the radiation of UV light, the energy transfer in Eu complexes and other compounds has been discussed.[4] Porphyrin derivatives, the main chromophores of natural photosynthesis, have attracted much attention not only from a fundamental point of view but also from their potential applications.[5] Recently, some amphiphilic metal complexes have been transferred onto solid substrates as mixed or alternate films, and the fluorescence quenching or columinescence properties have been reported.[6]

Previously, we have investigated the monolayer behaviors of some lanthanoid complexes and discussed their emission properties in LB films.[2,7] In the present paper, monolayers of europium (III) complexes and a porphyrin derivative were investigated, and the energy transfer between them in alternate LB films was discussed.

EXPERIMENTAL

Europium oxide (99.99%) was purchased from Yue Long Chemical Plant (Shanghai). Dibenzoylmethane (DBM) and N,N-dimethyldipalmitylammonium bromide [$(C_{16})_2NBr$] were from Tokyo Kasei Co., LTD., and tetrahexadecylammonium bromide [$(C_{16})_4NBr$] and stearic acid (SA) from Aldrich Chem. Co.

Europium complexes $(C_{16})_nNEu(DBM)_4$ and a porphyrin derivative (TSPP) shown in Figure 1 were synthesized and characterized according to the literature methods.[2,8]



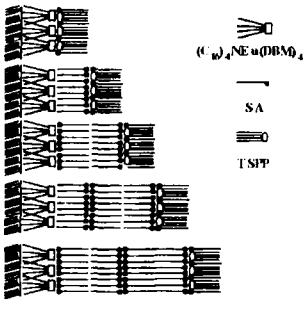


FIGURE 1 The compounds used in this work.
FIGURE 2 Schematic diagram of the LB films used for energy transfer investigations.

The monolayers were spread from chloroform solutions onto twice distilled water (deionized) surface or the surface of a subphase containing the associated Eu complex-ions, which was prepared by adding the $EuCl_3$ solution to DBM anion in the molar ratio of 1:4. The π-A isotherms were measured by a NIMA 2000 round trough at about 20 °C. Monolayers were transferred onto the hydrophobic quartz and glass plates with the patterns as shown in Figure 2. The UV-vis and fluorescence spectra were measured by Hewlett Packard models 8451A and Hitachi 850 spectroscopes, respectively. X-ray diffraction patterns were obtained by using a D/Max-γB X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm).

RESULTS AND DISCUSSION

Figure 3 (A) shows the π-A isotherms for the monolayers of Eu complexes and TSPP on water and the subphase surfaces, indicating that all of these compounds can form stable monolayers. However, it is confirmed that $(C_{16})_nNEu(DBM)_4$ complexes (especially for $n \leq 2$) can slightly dissolve into water, so a subphase of $KEu(DBM)_4$ was used in this work to prevent the dissolution of the complexes. Monolayers with higher collapse surface pressures and larger limited molecular areas are formed for $(C_{16})_nNEu(DBM)_4$ on the Eu complex-ion subphase surface in comparison with those on pure water

surface. These results can be attributed to the inhibition of the dissolution of the complexes and to the interaction between long chain ammonium of Eu complexes on the monolayers and the associated Eu complex-ion in the subphase. Figure 3 (B) shows the π-A isotherms for the mixed monolayers of TSPP and SA in different molar ratios, indicating that the condensed monolayers are formed.

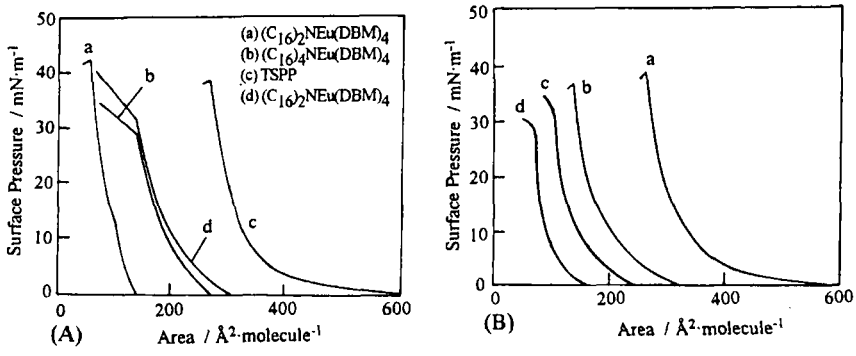


FIGURE 3 (A) π-A isotherms of the compounds on (a-c) water and (d) Eu complex-ion subphase surfaces.
(B) π-A isotherms of TSPP/SA in the molar ratio (a) 1:0, (b) 1:1, (c) 1:2 and (d) 1:4.

The monolayers of Eu complexes were transferred onto solid substrates alternatively with TSPP/SA (molar ratio, 1:4). The separation distances between the emission groups of complexes $(C_{16})_nEu(DBM)_4$ and the rings of TSPP are estimated by SA multilayers (Figure 2). The linear dependence of absorption intensity of the maximum peak for UV-vis spectra of the monolayer assemblies on the layer number suggests the homogeneous LB films. The result of X-ray diffraction indicates a periodical layer structure of the films. The layer space for the alternate multilayers of one layer $(C_{16})_4NEu(DBM)_4$ and one layer TSPP/SA is about 49 Å.

The fluorescence emission spectra for the monolayer assemblies both of Eu complex alone and of the complex alternately deposited with TSPP/SA show the emissions of Eu^{3+} ion corresponding to $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions.[2,4] A hypersensitive transition is $^5D_0 \rightarrow {}^7F_2$,[9] which is used to study the effect of TSPP on the fluorescence of Eu complexes. As shown in Figure 4, the emission from complex $(C_{16})_4NEu(DBM)_4$ is quenched to about 30% of the original intensity when it is directly contacted with a layer of TSPP/SA, and to be about 70% when the separation distance is about 25 Å (one layer of SA). This may be ascribed to an energy transfer from an excited state of europium (III) complexes to TSPP. When the separation distances are over 75 Å, the emissions of Eu complexes in alternate films are approximately to the original intensity.

According to the energy transfer processes of europium complexes,[10] the excited ligand DBM is deactivated by transferring the energy to Eu^{3+} ion through the triplet state of DBM (~20,400 cm^{-1}). UV-vis spectra for the complexes in LB films indicate that the maximum peaks are at about 252 and 352 nm, and for TSPP it is about 424 nm. The fluorescence emission bands for Eu^{3+} ion are most probably appeared at the range of 550 ~ 750 nm. Therefore, it is suggested that under UV radiation, the excited ligand DBM is mainly deactivated by two ways: one is to transfer the energy from singlet state (S_1) to triplet state (T_1), then to the excited state of Eu^{3+} ion followed by a fluorescence emission; another is to transfer the energy (S_1 state) to TSPP within a given region.

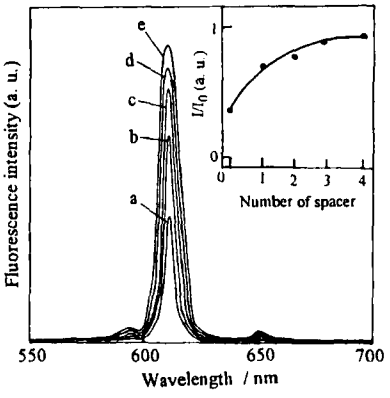


FIGURE 4 Emission spectral change in alternate films of $(C_{16})_4Eu(DBM)_4$ and TSPP/SA with the numbers of spacer layers (SA): (a)0, (b)1, (c)2, (d)3, and (e) $(C_{16})_4Eu(DBM)_4$ alone.

In conclusion, we have demonstrated an energy transfer between Eu complexes and a porphyrin derivative in their alternate LB films, and estimated the critical transfer distance to be about 75 Å.

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