Monolayer Assemblies of Long-chain Complex Containing Rare-earth Metal : *N,N*-Distearyldimethylammonium Tetra (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono) Europate(III)

Dongjin Qian, Hiroo Nakahara, Kiyoshige Fukuda, and Kongzhang Yang†
Faculty of Science, Saitama University, Urawa 338
†*Institute of Colloid and Interface Chemistry, Shandong University, Jinan, 250100, P. R. China*

(Received December 2, 1994)

Monolayers of a newly synthesized long-chain complex of europium(III) and its mixtures with octadecane or arachidic acid were investigated. Using the conventional LB and horizontal methods, the mixed monolayers could be deposited on solid supports. For the complex in monolayer assemblies, the emission probabilities from higher excited state $^5D_1$ than $^5D_0$ were remarkably enhanced in comparison with those in the solution or crystalline.

Since Waissman (1942) first reported that europium(III) complexes with β-diketone ligands exhibited line-like emissions and especially through the advance of laser spectroscopy, the emission behaviors of various europium (III) complexes and their applications as photochemical devices have been studied.[1,2] The Langmuir-Blodgett and the horizontal lifting methods offer valuable ways to arrange functional molecules in a purposely and highly ordered structure at ordinary temperatures and atmospheric pressures.[3,4] Recently, Huang et al reported second harmonic generation for the LB films of europium hemicyanine complex.[5] Previously, the authors studied on LB films of luminescent rare-earth chelates.[6] In this paper, a long-chain complex of europium (III) has been newly synthesized and the optical properties of the complex in the monolayer assemblies have been examined in comparison with those in the solution and crystalline.

The complex of N,N-distearyldimethylammonium tetra (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono) europate (III) $[(C_{18}H_{37})_2N(CH_3)_2Eu(TTA)_4]$ shown in Figure 1 was synthesized by Bauer et al's method[7] and recrystallized from a mixed solution of methanol and ethanol (1:1, v/v). The complex is pale yellow powders with the melting point of 86.5~86.7 °C. The results of elementary analysis were: C: 53.03 (calculated value 52.95), H: 6.02 (6.09), and N: 0.93 (0.88).

Monolayers of the Eu complex were spread from the chloroform solution onto the surface of distilled water and the surface pressure-area (π-A) isotherms were measured by a Lauda film balance. As shown in Figure 2, the π-A isotherms of the complex exhibit stable condensed monolayers in the temperature range of 8.5 ~ 30 °C. The molecular areas obtained by extrapolating the linear part to zero pressure fall into the range of 107 ~ 111 Å^2. These values are considered to correspond to the area of the large head group of the complex by comparing with the π-A isotherm of N,N-distearyldimethylammonium bromide (Figure 2, f), and by taking account of the crystallographic structure[8] of an analogous complex $C_7H_{10}NEu(TTA)_4$. With increasing the temperature, the collapse pressure tended to become higher with less compressibility of the monolayer.

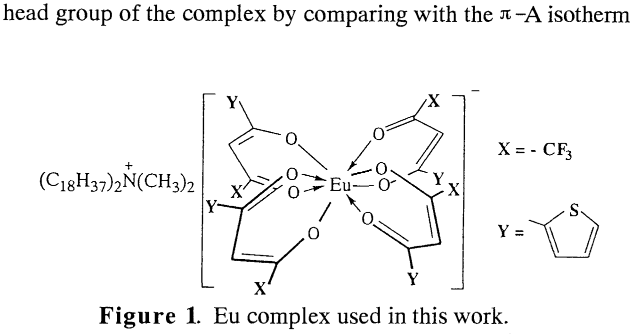

Figure 1. Eu complex used in this work.

The π-A isotherms for mixed monolayers of the Eu complex with octadecane (C18) at 20 °C are shown in Figure 3. It can be seen that the collapse pressures become higher with increasing molar fraction of C18, and C18 molecules added up to molar ratio 1:2 give scarcely any contribution to the area increase. These facts suggest that the molecules of C18 assist close packing of the alkyl chains of the complex having a large head group.

Mixtures of the Eu complex with arachidic acid (AA) also gave stable condensed monolayers. Monolayers of the complex alone and its mixtures with AA in the molar ratios of 2:1~1:12 were difficult to be transferred onto solid plates as ordered assem-

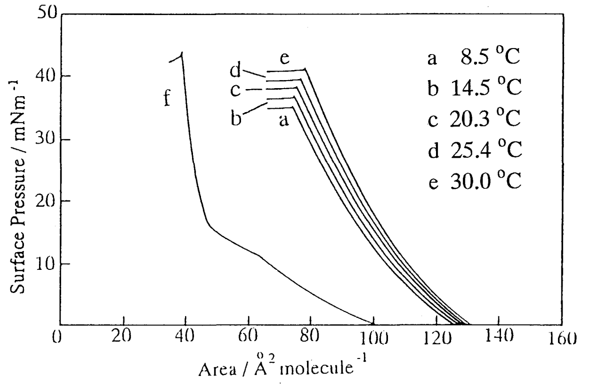

Figure 2. π-A isotherms of $(C_{18}H_{37})_2N(CH_3)_2Eu(TTA)_4$ at different temperature. f: $(C_{18}H_{37})_2N(CH_3)_2Br$ (20.3 °C).

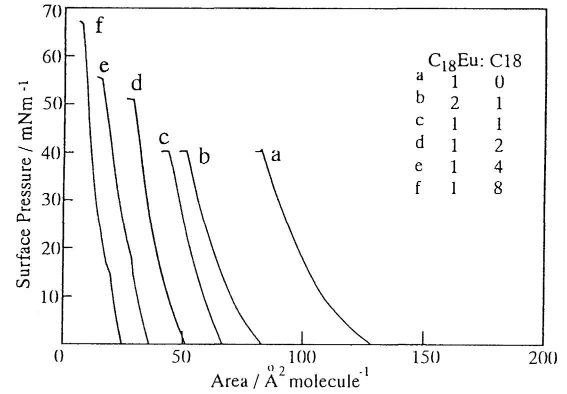

Figure 3. π-A isotherms for the mixed monolayers of the Eu complex ($C_{18}Eu$) with C18 at 20 °C.

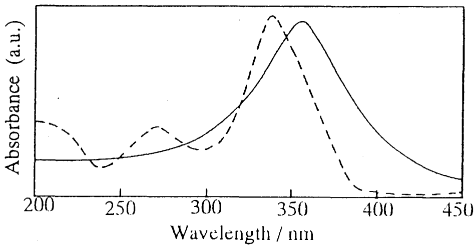

Figure 4. Absorption spectra of the Eu complex in multilayer mixed with C18 (——) and in methanol solution (----).

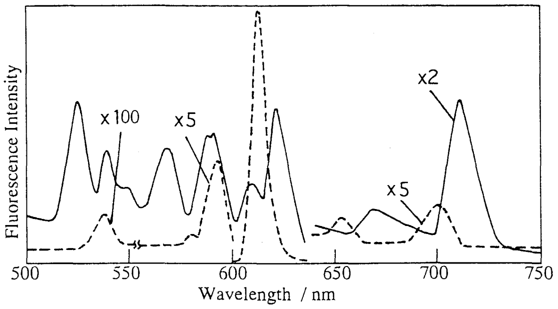

Figure 5. Fluorescence spectra of the Eu complex in multilayer mixed with C18 (——) and in chloroform solution (----).

blies over 10 layers, while mixed monolayers with AA in the molar ratios 1:16 (or more) could be deposited by LB method at 30 mNm^{-1} to form Y-type multilayers. On the other hand, the mixed monolayers of the complex with C18 in the molar ratio 1:4 could be transferred onto quartz plates, precoated with cadmium stearate layers to make a hydrophobic surface, by the horizontal lifting technique at 20 mNm^{-1} because of lack of the hydrophilicity for the C18 molecule. Figure 4 shows the absorption spectra for 50 layers of the Eu complex mixed with C18 (1:4) as compared with the solution spectrum of the complex. The metal ligand charge transfer (MLCT) band in the monolayer assemblies was shifted to longer wave-length and broadened in comparison with that in the methanol solution.

The fluorescence spectra of the Eu complex in the multilayers mixed with C18 (1:4) and the chloroform solution, excited at 398 nm,[9] are shown in Figure 5. The main emission wavelengths together with their assignments are listed in Table 1. For many europium(III) complexes in the literatures,[1,2,11] the fluorescence emissions in the solutions and crystallines are mainly $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions and the hypersensitive transition is $^5D_0 \rightarrow {}^7F_2$ at room temperature. In the multilayers, however, the transitions of both $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ and $^5D_1$ (higher excited energy state)$\rightarrow {}^7F_{0,1}$ were obviously observed, and further the $^5D_0 \rightarrow {}^7F_2$ transition in the monolayer assemblies splitted into two levels at about 615 and 625 nm, and the transition $^5D_0 \rightarrow {}^7F_1$ also slightly splitted and appeared at 590 ~ 593 nm. This may be ascribed to the fact that the complex in the monolayer assemblies are of highly ordered and close packed structure which leads to the decrease of thermal deactivation of the excited states as well as a slight distortion in the symmetry of the Eu complex and the enhancement of the emissions from $^5D_1$, though a weak emission from $^5D_1$ was also observed both in the crystalline and solution.

Table 1. Emission wavelengths (nm) of the Eu complex in multilayer, $CHCl_3$ solution and crystalline[10] at room temperature

multilayer(nm)	$CHCl_3$ solution(nm)	crystalline(nm)	assignments[11]
526	—	534	$^5D_1 \rightarrow {}^7F_0$
539	538	539	$^5D_1 \rightarrow {}^7F_1$
571	580	580	$^5D_0 \rightarrow {}^7F_0$
590 ~ 593	594	588, 595	$^5D_0 \rightarrow {}^7F_1$
613, 625	613	612, 614	$^5D_0 \rightarrow {}^7F_2$
669	654	657	$^5D_0 \rightarrow {}^7F_3$
712	702	696, 706	$^5D_0 \rightarrow {}^7F_4$

In conclusion, it has been found that in the monolayer chains the emission probabilities from higher excited state $^5D_1$ than $^5D_0$ were enhanced in comparison with those in the solution or crystalline. It can be suggested that ordered ultrathin films of luminescent europium (III) complexes provide not only a way for developing photochemical devices of molecular dimension, but also an alternative route to research the $^5D_1$ excited states of the europium(III) ion.

One of the author(D.Q.) expresses his gratitude to the Ministry of Education, Science and Culture of Japan for the financial support of his study at Saitama University.

References and notes

1 G. E. Buono-core and H. Li, *Coord. Chem. Rev.*, **99**, 55 (1990).
2 N. Sabbatini and M. Guardigli, *Coord. Chem. Rev.*, **123**, 201 (1993).
3 H. Nakahara, *New Functionality Materials, Volume C: Synthetic Process and Control of Functionality Materials*, 481 (1993).
4 H. Nakahara and K. Fukuda, *Thin Solid Films*, **99**, 430 (1983); **133**, 1 (1985); **160**, 153 (1988); **178**, 361 (1989).
5 D. J. Zhou, C. H. Huang, K. Z. Wang, G. H. Xu, X. S. Zhao, X. M. Xie, L. G. Xu and T. K. Li, *Langmuir*, **10**, 1910 (1994).
6 D. Qian and K. Yang, *Acta Phys.-Chim.*, **9**, 148 (1993).
7 H. Bauer, J. Blanc and D. L. Ross, *J. Am. Chem. Soc.*, **86**, 5125 (1964).
8 C. H. Huang, X. Y. Zhu, F. Y. Guo, J. Q. Song, Z. H. Xu, C. S. Liao and Z. S. Jin. *Acta Scientiarum Naturalium, Universitatis Pekinensis,* **28**, 428 (1992).
9 The action spectra for the complex in the multilayer and solution show the maximum at about 398 nm.
10 The fluorescence emission of the complex in crystalline were measured by use of its mixture with KBr (1:5000, w/w).
11 D. Qian, Z. Chen, S. Zhang and J. V. Houten, *Polyhedron*, **12**, 2763 (1993).