# A Luminescent Samarium Complex in Ring Microstructure in LB Films

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$Sm(TTA)_3Phen$ domains in a ring pattern were assembled by the Langmuir–Blodgett (LB) film technique. The domain pattern was observed by Brewster angle microscopy (BAM) at air/liquid interface and by atomic force microscopy (AFM) on mica. Under the electrostatic forces, $Sm(TTA)_3Phen$ molecules move towards and nucleate at the edge of the stearic acid (SA) domains exhibiting gradient electric field, resulting in the formation of ring domains of the samarium complex.

Rare earth complexes have been studied since the first half of 20th century.[1–4] With the rapid development of Langmuir–Blodgett (LB) film in the past 20 years, the complexes begin to be studied by using this method at the molecular level,[5–8] as what has been done for other compounds, especially biological molecules.[9–12]

A lot more significant work about microstructure should be carried out in the LB film, since it is a powerful technique at the molecular level. However, previous studies about rare earth complexes in the LB film were concentrated on the novel fluorescence character, intermolecular and intramolecular energy transfer schemes.[5–8,13,14] From the viewpoint of material science, molecular distribution has a close relationship with the macroscopic property. Many methods including external electric field[15,16] have been sought to achieve certain domain shapes. This paper addresses an easy method to get regular ring domains of $Sm(TTA)_3Phen$ (TTA denotes thenoyltrifluoroacetone; Phen denotes 1,10-phenanthroline.) with intense fluorescence emission by adjusting several factors involving in the fabrication process of the LB film. The interaction between samarium complexes and stearic acid (SA) in the double-component LB films is also addressed in this work. The results will be helpful for practical application in areas relating to ultrathin luminescence devices as well as anti-forgery techniques.

At the beginning of compression, no textures could be observed in the $Sm(TTA)_3Phen$/SA (in a molar ratio of 1:1) monolayer. When surface pressure reached 3 mN·m$^{-1}$, round black domains began to form (Figure 1a). At 9 mN·m$^{-1}$, bright ring domains generating at the edge of round domains could be distinguished (Figure 1b). Then ring domains grew thicker and thicker. Finally, they stopped growing and packed closely (Figure 1c). The inner black domains had a diameter range of 3–20 μm, the bright ring domains had a thickness about 2 μm.

It is well known that, for Brewster angle measurement (BAM), difference of reflected light intensity from air/liquid interface implies the existence of different phases. The bright ring domains and the black core domains should be made of different phases. Surface-pressure versus area per molecule (π–A) isotherms show that, a phase transition plateau appears at 9 mN·m$^{-1}$ in the $Sm(TTA)_3Phen$/SA (1:1) monolayer (Figure 1-I), corresponding to the formation of ring domains. Combining the fact that a similar plateau appears in the $Sm(TTA)_3Phen$ monolayer (Figure 1-II), it can be deduced that, the ring domains are made of $Sm(TTA)_3Phen$, and the inner round domains are made of SA. Due to the similar physical property between Eu(III) and Sm(III) since they are in the lanthanide series,[17] the result in this paper is consistent with our previous study on the assignment for ring/core microstructure in $Eu(TTA)_3Phen$/SA (1:1) monolayer,[18] where the ring domains are assigned to $Eu(TTA)_3Phen$ by fluorescence microscopy (FM). Since $Sm(TTA)_3Phen$ emits much weaker fluorescence than $Eu(TTA)_3Phen$ in monolayer at air/liquid interface, the fluorescence could not be photographed and shown.

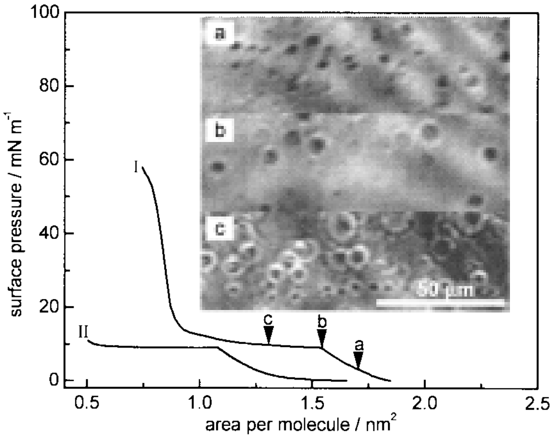

**Figure 1.** π-A isotherms of (I) $Sm(TTA)_3Phen$/SA (in a molar ratio of 1:1) and (II) $Sm(TTA)_3Phen$ monolayer at air/liquid interface on a composite subphase. The insets are BAM micrographs of $Sm(TTA)_3Phen$/SA (1:1) monolayer at (a) 3 mN·m$^{-1}$; (b) 9 mN·m$^{-1}$ and (c) 9.5 mN·m$^{-1}$.

When increasing the molar ratio of SA to $Sm(TTA)_3Phen$/SA = 1/6, ring domains of $Sm(TTA)_3Phen$ with the thickness of 2 μm could still be observed surrounding bigger SA round domains in the diameter range of 5–50 μm. However, when decreasing the SA ratio, ring domains could not be observed.

No ring domains could be observed for mixed monolayers of $Sm(TTA)_3Phen$ with SA in a molar ratio of 1:1 on a pure water subphase, because only a little samarium complex remains in the monolayer due to its dissolution and dissociation in water. As a result, we prepared composite subphases with saturated $Sm(TTA)_3Phen$ and the ligands to assure the stable existence of the samarium complex in the monolayer at air/liquid interface.

The $Sm(TTA)_3Phen/SA$ (1:1) monolayer could be transferred onto solid substrates by a horizontal lifting method with well-kept ring domains. Figure 2 shows the AFM micrograph of $Sm(TTA)_3Phen/SA$ (1:1) on mica transferred from the monolayer at a surface pressure of 9.5 $mN{\cdot}m^{-1}$. Three areas can be clearly recognized: the ring domains made of $Sm(TTA)_3Phen$; the inner round domains made of SA, and the matrix part made of the mixture of $Sm(TTA)_3Phen/SA$. The defects in this image are attributed to the dewetting effect of the monolayer when the LB film is air/dried. Combining the fact that $Sm(TTA)_3Phen$ itself could not be transferred well onto solid substrate if the monolayer did not contain SA,[6,7] it can be deduced that, SA in the double-component system not only triggers $Sm(TTA)_3Phen$ to form ring domains, but also helps the complex to transfer onto solid substrates.

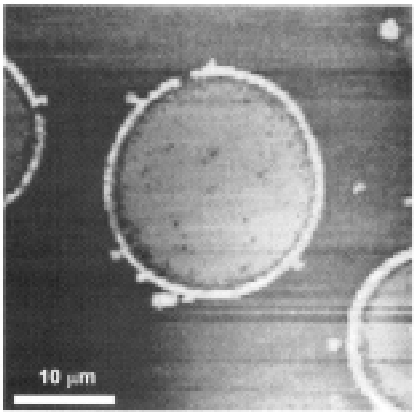

**Figure 2.** AFM micrograph of $Sm(TTA)_3Phen/SA$ (in a molar ratio of 1:1) on mica. The surface pressure during transfer from the monolayer at air/liquid interface is 9.5 $mN{\cdot}m^{-1}$.

The formation scheme of $Sm(TTA)_3Phen$ ring domains is discussed as follows. When the SA molecules in gaseous state in the monolayer come closer enough to each other, the interaction between the aliphatic chains attract SA molecules together, corresponding to a nucleation process of SA domains. Then the diameter of SA domains increases with the joining of neighbor SA molecules in the mixture of SA and $Sm(TTA)_3Phen$. During the formation process of SA domains, $Sm(TTA)_3Phen$ molecules in matrix area come closer to SA domains. As we know, SA domains exhibit electric gradient field resulting from the highly ordered orientation of SA molecules with dipole moment.[19,20] Moreover, the $Sm(TTA)_3Phen$ molecules is an asymmetric molecule with a dipole moment of 4 D calculated by a MOPAC semi-empirical program. Under the electric gradient field of SA domains, nucleation of $Sm(TTA)_3Phen$ takes place at the prefer site — the edge of SA domains at the air/liquid interface. With decrease of monolayer area, the $Sm(TTA)_3Phen$ molecules compressed close enough to the ring domains will join them. With the growth of ring domains, the electric gradient field of SA domains is gradually weakened so that $Sm(TTA)_3Phen$ molecules will not join them further, resulting in the termination of ring domain growth.

## References

1 E. H. Huffman, *Nature*, **200**, 158 (1963).
2 J. G. White, *Inorg. Chim. Acta,* **16**, 159 (1976).
3 S. Sato and M. Wada, *Bull. Chem. Soc. Jpn.*, **43**, 1955 (1970).
4 G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, **34**, 743 (1961).
5 R. J. Zhang and K. Z. Yang, *Langmuir*, **13**, 7141 (1997).
6 R. J. Zhang, H. G. Liu, K. Z. Yang, Z. K. Si, G. Y Zhu, and H. W. Zhang, *Thin Solid Films*, **295**, 228 (1997).
7 R. J. Zhang, H. G. Liu, C. R. Zhang, K. Z. Yang, G. Y. Zhu, and H. W. Zhang, *Thin Solid Films*, **302**, 223 (1997).
8 H. Li, C. H. Huang, X. S. Zhao, X. M. Xie, L. G. Xu, and T. K. Li, *Langmuir*, **10**, 3794 (1994).
9 A. Miller, W. Knoll, and H. Möhwald, *Phys. Rev. Lett.*, **56**, 2633 (1986).
10 C. M. Knobler, *Science*, **249**, 870 (1990).
11 M. Lösche, E. Sackmann, and H. Möhwald, *Ber. Bunsen-Ges. Phys. Chem.*, **87**, 848 (1983).
12 L. F. Chi, R. R. Johnstan, N. Kimizuka, T. Kunitake, and H. Ringsdorf, *Langmuir*, **8**, 1360 (1992).
13 R. J. Zhang, K. Z. Yang, A. C. Yu, and X. S. Zhao, *Thin Solid Films*, **363**, 275 (2000).
14 R. J. Zhang and K. Z. Yang, *Acta Chimica Sinica*, **58**, 748 (2000).
15 T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, and H. M. Jaeger, *Science*, **273**, 931 (1996).
16 K. Amundson, E. Helfand, X. Quan and S. D. Smith, *Macromolecules*, **26**, 2698 (1993).
17 N. M. Edelstein, "Lanthanide and Actinide Chemistry and Spectroscopy", American Chemical Society, Washington D.C., 1980.
18 R. J. Zhang, P. Krüger, B. Kohlstrunk, K. Z. Yang, and M. Lösche, Submitted to *Chem. Phys. Chem.*
19 H. M. McConnell and V. T. Moy, *J. Phys. Chem.*, **92**, 4250 (1988).
20 H. Möhwald, S. Kirstein, H. Haas, and M. Flörsheimer, *J. Chim. Phys.*, **85**, 1009 (1988).