Langmuir-Blodgett film formation of rare-earth metal di-, triphthalocyanine complexes and observation of their thin film by means of TEM and STM

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Abstract Three different kinds of rare-earth metal phthalocyanine complexes (Pc_2LuH, Pc_3Gd_2, R_{12} Pc_3Dy_2) were synthesized. Their ultra-thin films were prepared by the Langmuir-Blodgett technique. Crystallites were observed in Langmuir film of Pc_3Gd_2 by means of transmission electron microscopy. The limiting molecular areas of the phthalocyanine derivatives on pure water increased in the order mono-, di- and triphthalocyanine, implying that these phthalocyanine molecules are stacked with a face-to-face orientation and edge-on to the water surface. By using scanning tunneling microscopy individual molecules of lutetium diphthalocyanine adsorbed on graphite surfaces were imaged for the first time.

Introduction

Rare-earth metal diphthalocyanine complexes have received much attention over the past years due to their potential application in color display devices and as camouflage materials. These compounds exhibit reversible color change, either in solution or as a thin film, from original green to red-brown in the oxidation process, and through blue to purple in the reduction process. As the rare-earth metal diphthalocyanine complexes are typical molecular semiconductors, semiconductor devices such as Schottky junctions, p-n junctions, bipolar transistors, field-effect transistors, etc., may be prepared.

The Langmuir-Blodgett (L-B) technique is a very useful method for fabricating ultrathin films without defects. In recent years much effort has been made to improve the solubility of phthalocyanine complexes by modifying the nature of the substituents on the periphery benzo-ring in the hope to meet the precondition of L-B method.

Scanning tunneling microscopy (STM) has emerged as an important technique for real-space imaging of surfaces. Although the sandwich structure of rare-earth metal diphthalocyanines is widely accepted, it is nevertheless significant if individual molecules of these complexes could be imaged using STM.

In this paper, the syntheses of three different kinds of phthalocyanine derivatives, *i.e.*, lutetium diphthalocyanine (Pc_2LuH), gadolinium triphthalocyanine (Pc_3Gd_2) and dysprosium

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dodecapropoxy triphthalocyanine ($R_{12}Pc_3Dy_2$) are described. Their formation into L-B films, as well as their direct characterization by transmission electron microscopy (TEM) and STM are also described.

Experimental

Synthesis

We have described the syntheses and purification of substituted and unsubstituted rare-earth metal diphthalocyanine derivatives in an earlier publication.[1] The synthetic scheme is as follows (Fig. 1): phthalonitrile and rare-earth acetate salt were heated in an evacuated glass tube to 290°C for 4 h. The crude products were separated by column chromatography (silica gel, 100 mesh-up, elution with $CHCl_3$), followed by drying under high vacuum (10^{-6} Torr, 250—260°C) for 1 h. When the mole ratio of phthalonitrile or 4-propoxyphthalonitrile

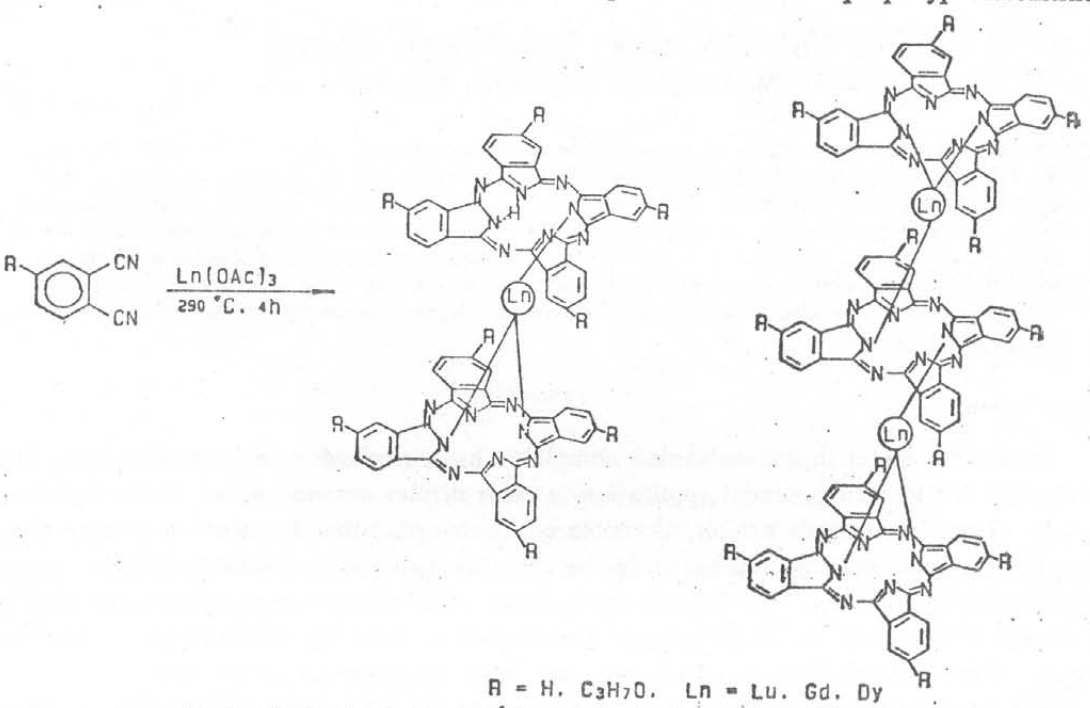

Fig. 1 Synthesis of dimeric and trimeric phthalocyanine derivatives

Table 1 Elemental analyses of rare-earth metal phthalocyanine complexes

Compounds	Anal. Calcd (Found)		
	C	H	N
Pc_2LuH	64.00 (63.50)	2.77 (2.65)	18.66 (18.20)
Pc_3Gd_2	62.26 (61.76)	2.61 (2.59)	18.1 (17.55)
$R_{12}Pc_3Dy_2$	61.94 (62.57)	4.73 (4.77)	13.13 (13.06)

to rare-earth acetate was equal to 6, a small amount of trimeric complex was obtained as a by-product in addition to the dimer. Results of elemental analysis of these compounds are listed in Table 1.

L-B film formation

Solutions of the phthalocyanine derivatives in chloroform were prepared by ultrasonic agitation for 30 min to ensure complete dissolution. The solutions were spread on the surface of pure water (ca. pH=6, 21°C). The surface pressure-area isotherms (FA) were measured by compressing the mobile barrier. The Langmuir films were transferred to the substrates at a constant surface pressure of 20 mN / m by the vertical dipping (VD) method at a substrate up-down speed of 5 mm / min. The substrates were either conducting glass, quartz or optical glass.

Instrumentation and measurement

The L-B films were prepared with a KSV 5000 apparatus. The photographs of TEM and STM were obtained with a Hitachi Transmission Electron Microscopy and a home-made Scanning Tunneling Microscope with computer data-acquisition.

Results and discussion

FA isotherms and L-B films

The FA isotherms of Pc_2LuH, Pc_3Gd_2 and $R_{12}Pc_3Dy_2$ are shown in Fig. 2. The limiting molecular areas were determined to be ca. 77.4 Å², 138 Å² and 257.8 Å² respectively by extrapolating the steeply rising part of the isotherm to zero surface pressure. As we know the limiting molecular area of monophthalocyanine obtained by experiment is ca. 30 Å², the diagonal distance across the molecule of unsubstituted phthalocyanine is 13.2 Å, and the "thickness" of the mono- and diphthalocyanine molecules are 3.4 Å and 8.45 Å given by X-ray analysis. If the phthalocyanine molecules are densely stacked by face-to-face orientation and edge-on to the water surface the limiting molecular areas for the mono- and di-phthalocyanine, should be 31.7 Å² and 78.8 Å², products of side 9.33 Å ($13.2 \times \frac{1}{2}\sqrt{2}$) times the thickness 3.4 Å and 8.45 Å respectively, which obviously conform with the experimental

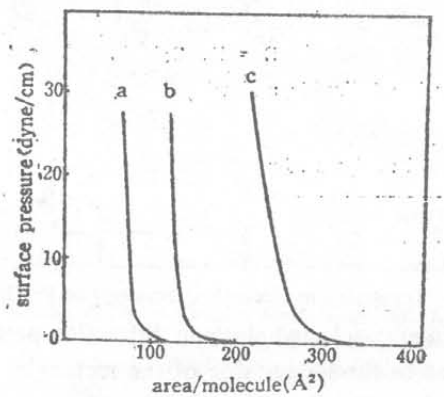

Fig. 2 Surface pressure-area isotherms of rare-earth metal phthalocyanine complexes
a: Pc_2LuH; b: Pc_3Gd_2; c: $R_{12}Pc_3Dy_2$

data. Note that this assumption seems reasonable because of another experimental fact, *i.e.* the limiting molecular area increases in order from mono-, to di- to tri-phthalocyanine, if the phthalocyanine derivatives floated on the water surface, their limiting molecular areas should all have the same value of 87 Å^2. We lack X-ray analytical data on triphthalocyanine at present moment, it is difficult to calculate its molecular dimension. As a result of R-substitution the increment of side length of the molecules makes the limiting molecular area of $R_{12}Pc_3Dy_2$ increase to 257.8 Å^2.

In normal cases, the concentration suitable for L–B fabrication is of the order of 10^{-1} mmol / L, and the amount of solution evaporated on the water surface is less than 0.2 mL. Unsubstituted mono-phthalocyanines are difficult to fabricate into L–B films because of their poor solubility, with the exception of lithium phthalocyanine. Although a few unsubstituted diphthalocyanines can be fabricated by the L–B technique, 0.5 mL or even more of the solution is needed during the deposition owing to their comparatively lower concentration. However, the substituted phthalocyanines exhibit much better solubility than that of unsubstituted ones. From this point of view, our substituted mono-, di- or tri-phthalocyanines were found to be good L–B film-forming materials.

Transmission electron microscopy (TEM)

The sample of Pc_3Gd_2 for TEM was prepared by transferring one layer of its Langmuir film onto a carbon-covered copper net. Under TEM some rectangular 3-dimensional crystallites with maximum size of ca. 0.38×0.25 μm, shown in Fig. 3, were observed. Two

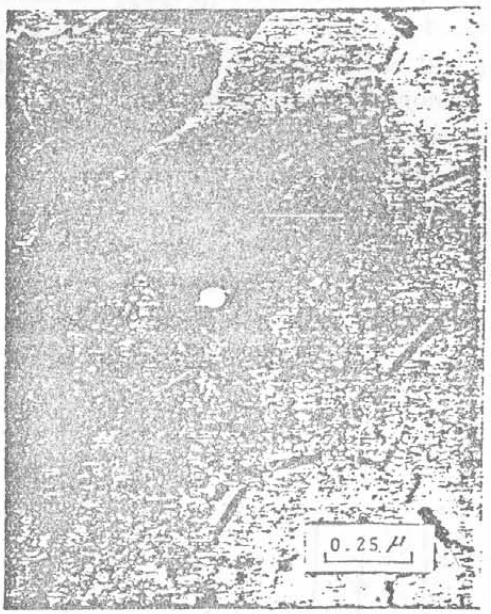

Fig. 3 Transmission electron microscopy of Pc_3Gd_2

diffraction points were found in area-selected electron diffraction pattern and the line linking up the two points is perpendicular to the longer side of the rectangle. Ayrapetiants S.V. *et al.*[3] investigated L–B films of stearic acid using EM, and found that monoclinic crystallites grew when the film thickness increased approximately up to 10 monolayers. In our case, the

crystallites were found in Langmuir films. M'Sadak M. *et al.*[3] proposed that the complex Pc_3Ln_2 can be represented as $(Pc_2Ln)^-(PcLn)^+$, which can hydrolyze in a protic medium according to the following scheme:

$$(Pc_2Ln)^-(PcLn)^+ \xrightarrow{H_2O} Pc_2LnH + PcLn(OH) \xrightarrow{H_2O} PcH_2 \quad (1)$$

As we know, the solubilities of the mono- and di-phthalocyanines are poorer than that of tri-phthalocyanine, so that crystallites observed in Langmuir films may be the result of decomposition of the tri-phthalocyanine. In our previous work[4] on substituted phthalocyanines, high quality L–B films were obtained easily. These experimental facts suggest that the substituents at the peripheral benzo-ring not only improve their solubility but also decrease their crystallinity, which plays an important role in the preparation of L–B films.

Images of Pc_2LuH adsorbed on graphite surface by STM

STM measurements were calibrated using a graphite surface which exhibited a characteristic atomic-resolution pattern of threefold symmetric minima separated by 2.46 Å. At first we tried the L–B film of Pc_2LuH but failed to obtain a clear picture. Then we succeeded by dropping a dilute solution of Pc_2LuH on a graphite surface and put it on the sample holder of STM. The experimental details will be published in a separate paper.

As shown in Fig. 4, considerable molecular information is obtained: (1) the molecule has a ring structure with four segments, each segment corresponding to an isoindole unit (4c); (2) Pc_2LuH is a sandwich-type complex (4a, 4b); (3) the molecular size is ca.9×12Å, which is in good agreement with the X-ray analysis. These results demonstrate that individual molecules can be imaged by STM.

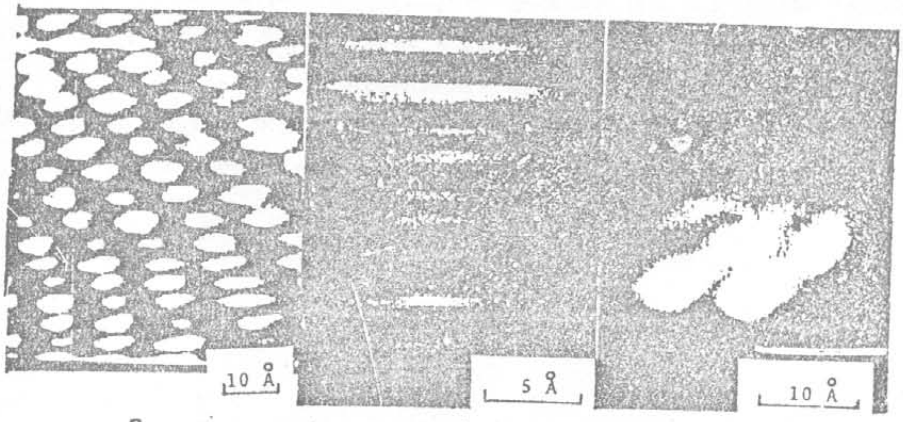

Fig. 4 Scanning tunneling microscopy images of Pc_2LuH
a: top view; b: side view; c: single phthalocyanine ring

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References

1. Liu, Y-Q.; Shigehara, K.; Yamada, A., *Acta Chimica Sinica Engl. Ed.*, 3, 209 (1989).
2. Ayrapetiants, S.V.; Bannikov, V.S.; Lvov, Yu. M.; Myagkov, I.V.; Sotnikov, P.S.; Troitskiy, V.I.; Feigin, L.A., *Proceeding of the 4th International School on Condensed Matter Physics, "Molecular Electronics,"* Varan, 18 27 September, 593 (1986).
3. M'Sadak, M.; Roncali, J.; Garnier, F., *J. Chim. Phys.*, 83(3), 211 (1986).
4. Liu, Y-Q.; Yamada, A.; Shigehara, K.; Hara, M., *Chn. J. Polym. Sci.*, 6(4) 289 (1988).