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Synthesis of soluble rare-earth metal bisphthalocyanines and their Langmuir–Blodgett films for gas sensibility

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Abstract

In the present work, the synthesis of octa-4-(2,4-di-tert-pentylphenoxyl)-substituted rare-earth bisphthalocyanine with Sm, Er and Nd as central metal atom, respectively, is described. These compounds have improved solubility in organic solvents, and can form homogenous and relatively stable films at the air/water interface. The Langmuir film can be transferred by vertical dipping onto substrates with Z-type configuration. In Langmuir–Blodgett (LB) films, rare-earth bisphthalocyanine molecules exist mainly in associated species. The absorption increases linearly with the number of deposited layers indicating reproducible quality, and the layers adhere tenaciously to substrates and to each other. The gas sensibility of the films was investigated. The LB films of Sm and Er bisphthalocyanines have sensibility for the vapors of NH_3 and NO_2, but that of Nd bisphthalocyanine exhibits sensibility and selectivity only for the vapor of NH_3.

Keywords: Rare-earth metal bisphthalocyanines; Synthesis; Langmuir–Blodgett films; Gas sensitivity

1. Introduction

Interest in the Langmuir–Blodgett (LB) technique has led to a number of investigations into different types of materials that can be deposited in the form of monomolecular layers. If LB films are to be used commercially, mechanical and thermal stability will be necessary. Recently, interest has focused on rare-earth bisphthalocyanine, a substance well known for its thermal and chemical stability, to produce LB films. The conductivities of this material and its derivatives are very sensitive to the presence of certain gases, which leads to an interest in their use as microelectronics gas sensors. Phthalocyanines are known as p-type semiconductors. The gas sensing is realized through the charge transfer interaction in which the gas molecule to be sensed acts as a planar π-electron acceptor forming a redox couple, and the positive charge produced is delocalized over the phthalocyanine ring causing the increase of conductivity.

$LuPc_2$ has been described as the first molecular semiconductor. The effects of NO_2 gas at room temperature on the conductivity of $LuPc_2$ layers produced by evaporation have been reported [1]. Rickwood [2] reported the electrical and chlorine-sensing properties of ytterbium (Yb) bisphthalocyanine LB thin films, after an investigation of temperature and atmosphere affecting the gas-sensing properties of Yb bisphthalocyanine.

Since gas adsorption is a surface phenomenon, it has been suggested that ultra thin films with a higher degree of surface uniformity can enable the gas molecules to absorb at or desorb from the molecular sites more readily. Deposition of thin films by the LB technique is a highly attractive method for producing well-ordered thin films of known thickness. Surface damage is inherent with high energy techniques such as sputtering or evaporation. The use of LB films at elevated temperature increases the probability of disintegration and distortion of the layered structure. Therefore, fabricating molecular layers by the room-temperature LB technique was expected to produce better gas sensitivity in many cases [3]. In fact, faster response and recovery time were observed for LB films with substituted phthalocyanine molecules when exposed to NO_2 than those reported for vacuum-evaporated film [4].

Other metal phthalocyanines have been scarcely explored. In this paper we report on the synthesis of rare-earth metal (Sm, Er and Nd) bisphthalocyanines, their monolayer behav-

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ior and the gas sensibility of their LB films for the vapors of NH_3 and NO_2.

2. Experimental details

All reagents and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted.

*2.1. Synthesis of 4-(2,4-di-t-pentylphenoxy)-1,2-dicyanobenzene (**I**)*

In nitrogen atmosphere, 9.0 g anhydrous K_2CO_3 were added to a solution of 3.0 g (17.34 mmol) 4-nitro-1,2-dicyanobenzene and 4.1 g (17.52 mmol) 2,4-di-t-phenol in 50 ml of dry Me_2SO by 3 g additions at 1 h intervals over an 3 h period. The mixture was stirred for 24 h at 40–50 °C under nitrogen, then cooled to room temperature. The reaction products were dumped into 500 ml ice–water, filtered and washed to neutral. The rude product was recrystallized from methanol, dried to yield to 3.9 g (61.6%); m.p. 99–101 °C. IR (KBr pellet cm^{-1}): 3100 w($\nu_{=C–H}$), 608 s($\nu_{C=C}$), 2237 m($\nu_{C\equiv N}$), 1536 s ($\nu_{as\text{-}NO_2}$), 1348 s($\nu_{s\text{-}NO_2}$), 2950 s, 900 sh, 2800 sh, 1391 ms, 1881 s, 1358 sh, 1306 s, 1276 sh, 948 w, 776 m (the characteristic band of tert-pentyl), 2218 sh, 1582 s, 1480 s, 818 sh (the characteristic band of 1,2.4-trisubstituted benzenyl).

*2.2. Synthesis of octa-4-(2,4-di-tert-pentylphenoxy) rare-earth metal (Sm, Er and Nd) bisphthalocyanine (R_8Pc_2Ln) (**II**)*

II was prepared according to the method described by Kiren [5]. **I** and rare-earth (Sm, Er and Nd) acetate (molar ratio, 8:1) were heated in a glass tube to 260 °C for 4 h under nitrogen. After cooling, the green solid product was milled and dissolved in chloroform. The solution was filtered and purified by column chromatography (alumina, +mesh, 3×40 cm, 10% $CH_3OH–CHCl_3$ solution). The second green band was collected and evaporated to dryness. The compounds were characterized by elemental analysis, IR and UV–Vis spectra.

Elemental analysis composition is shown in Table 1. Elemental analysis of the green compounds is consistent with the formula $LnPc'_2$.

Table 1
Elemental analysis composition [a] of rare-earth metal bisphthalocyanines

$LnC_{192}H_{225}O_8N_{16}$	C (%)	H (%)	N (%)
Ln = Sm	76.01 (75.37)	7.42 (7.45)	7.39 (7.55)
Ln = Er	75.58 (75.77)	7.38 (7.42)	7.35 (7.49)
Ln = Nd	76.17 (76.08)	7.44 (7.50)	7.40 (7.45)

[a] Composition found is in parentheses.

Infrared spectroscopy has been generally used to check the purity of phthalocyanine complexes, especially to detect H_2Pc, which shows as a characteristic band at 1008 cm^{-1} [6]. The lack of the 1008 cm^{-1} peak in the spectrum confirms the absence of H_2Pc. IR (KBr pellet cm^{-1}) for $NdPc'_2$: 747 w (ring deformation), 891 w (Pc), 1089 s (Pc ring), 1228.6 s ($\nu_{Pc\text{-}o}$) [7], 1316.5 w (pyrrole stretch), 1479.8 vs ($\nu_{PcC=N}$, $\delta_{C–C–N}$, pyrrole stretch), 1524.8 w ($\nu_{PcC=N}$, pyrrole stretch), 1608.9 m ($\nu_{PcC=C}$, benzene stretch) [8].

The other lanthanide (Sm, Er) phthalocyanine spectra are similar to the Nd bisphthalocyanine; we only observe a small shift to higher frequency.

2.3. Preparation of monolayer of rare-earth metal (Sm, Er and Nd) bisphthalocyanine

Rare-earth metal bisphthalocyanine was dissolved in chloroform. A given amount (350 μl) of 2.0×10^{-4} M R_8Pc_2Ln–$CHCl_3$ solution was spread on a freshly distilled water subphase (about pH 6.0) at 15 °C. A Wilhelmy plate was used to measure changes in the surface tension. After complete evaporation of the solvent, the monolayer was compressed by the use of a mobile Teflon barrier at a speed of 15 mm/min. Film pressure versus area/molecule curves were recorded simultaneously.

2.4. Preparation of LB films of rare-earth metal (Sm, Er and Nd) bisphthalocyanine

The optical absorption of the films deposited onto clear quartz substrates was determined using a Shimadzu 2100 UV–Vis spectrophotometer.

Measurement of conductivity in the presence of different gas mixtures was performed by depositing the phthalocyanine films onto a glass substrate which possessed an interdigital Al electrode pattern on its surface. Contact to both electrons was made using air-drying Ag paste. The resulting device was positioned in a purpose-built glass sample chamber through which a variety of gases were introduced.

The Al interdigital electrode consists of 50 finger pairs of electrodes having a width of 50 μm, spaced 50 μm from the adjacent electrode. The finger overlap distance was 10 mm.

These substrates were initially well washed with detergent, followed by freshly distilled water, methanol and chloroform using ultrasonic waves for 15 min each; then they were dried and immediately used.

The LB films were kept at a surface pressure of 20, 18 and 12 dyn/cm (Sm, Er and Nd bisphthalocyanine, respectively) for 30 min. When stability was reached, they were transferred onto the substrate by the vertical dipping method with Z-type configuration at a substrate up–down speed of 5 mm/min.

Deposition was Z-type with the substrate being passed through a clean water surface in one compartment and withdrawn through the monolayer in the other compartment. The deposition of a Z-type multilayer film has been established

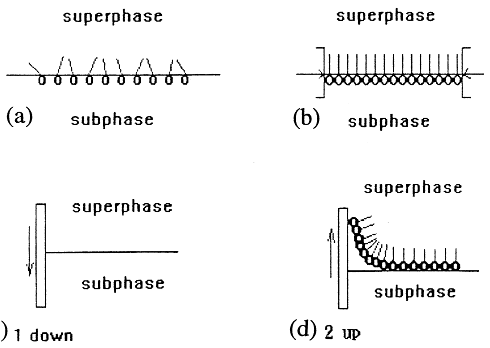

Fig. 1. LB film deposition of the Z-type: (a) molecules floating on the aqueous subphase following evaporation of volatile solvent; (b) molecules aligning as they are compressed by a moving barrier; (c) insertion of a suitable substrate; (d) transfer of floating layers withdrawal of a suitable substrate.

which yield deposition ratios of unity. LB film depositions of Z-type are shown in Fig. 1.

3. Results and discussion

3.1. Monolayer behavior

Surface pressure versus area isotherms of rare-earth metal (Sm, Er and Nd) bisphthalocyanine are shown in Fig. 2. Stable, reproducible LB films of these complexes were formed with a high collapse pressure, up to 63 dyn/cm for SmPc$'_2$, 56 dyn/cm for ErPc$'_2$ and 38 dyn/cm for NdPc$'_2$. Values for the average area per molecule of rare-earth metal bisphthalocyanine obtained by extrapolating the steeply rising part of the curve to zero pressure are approximately 125, 150 and 55 Å^2, respectively. The limiting molecular areas of LnPc$'_2$ are not equal regarding the central metal ions. The limiting molecular area is useful in guessing the configuration of the Pc molecule at the air/water interface. A full structure determination has not been carried out for LnPc$'_2$, and therefore it is difficult to be precise about the molecular dimensions. However, it is possible to make reasonable estimates. The area per molecule calculated by Liu et al. [7] is approximately 164.8 Å^2 if the molecules of LnPc$'_2$ are densely stacked in a face-to-face orientation and edge-on to the water surface. Since the calculated area per molecule is larger than the limiting molecular areas obtained by the experiment, we suggest that the Pc plane is tilted to the water surface.

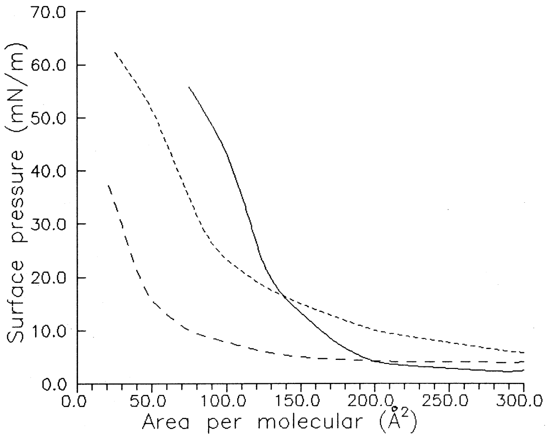

Fig. 2. Surface pressure vs. area isotherms of rare-earth metal bisphthalocyanines: ———— , NdPc$'_2$; - - -, SmPc$'_2$; ————, ErPc$'_2$.

The reproducibility of the isotherm is excellent and is limited only by the accuracy with which known amounts of LnPc$'_2$ can be applied to the trough. Hysteresis is also minimal during successive compressions and expansions of the floating monolayer. It is instructive to use polarized light to support the stacking hypothesis for our films (as will be published in a forthcoming article [9]). The isotherm shows that the monolayer can be compressed to a fully condensed close-packed film.

3.2. UV–Vis spectroscopic characterization

Fig. 3 shows a typical absorption spectrum of rare-earth metal bisphthalocyanine in LB films. The Q-band splits into two maximum peaks at 686 and 718 nm, and also the shoulder peak splits into 620 and 660 nm.

The single-crystal structure of Nd bisphthalocyanine without substitutes was analyzed by Kasuga et al. [10]. Other lanthanide sandwich compounds have essentially the same structure [11] in which the rare-earth ion occupies a central position between two parallel but staggered (45°) phthalocyanine ligands. While one of the phthalocyanine macrocycles is slightly saucer-shaped toward the rare-earth ion, the other is planar. The structure of the title complex is similar to this except that eight substituents of 2,4-di-tert-pentylphenoxy have been symmetrically connected to the two macrocycles. Thus, we can suppose that the structure of the title complex molecule is similar to the structure of the lanthanide bisphthalocyanine molecule without substitutes. The structure of our compound is shown in Fig. 4.

Because the two phthalocyanine macrocycles of the complex are slightly different to each other, the conjugated π bands of the two rings are not same. As mentioned above, π–π^* transitions observed in the electronic absorption spec-

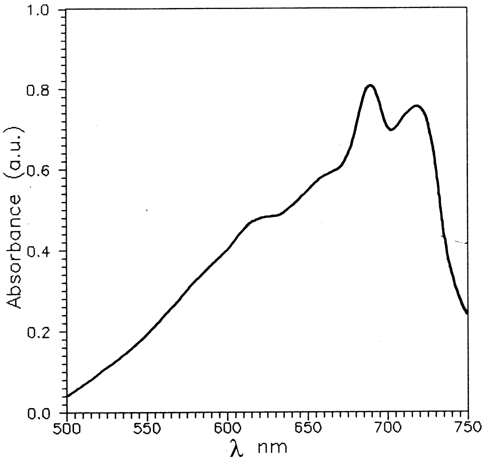

Fig. 3. UV–Vis spectrum of rare-earth metal bisphthalocyanine in LB films.

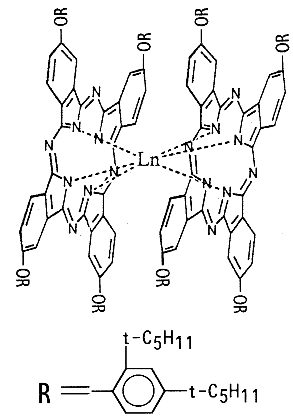

Fig. 4. Structure of rare-earth metal bisphthalocyanine.

trum can be separated into two pairs. Bands of 660 and 718 nm are assigned into π–π^* transitions of two phthalocyanine macrocycles, respectively. The 718 nm peak corresponds to the planar phthalocyanine π–π^* transitions, while the 686 nm peak corresponds to the saucer-shaped phthalocyanine macrocycle. Conjugativity of the saucer-shaped phthalocyanine macrocycle decreased because it is slightly out of plane compared with the planar one. Therefore, the absorption band is shifted to the blue direction. The weak peaks at 620 and 660 nm are due to the existence of a small amount of associated species in LB films.

Molecules are arranged closer compared with molecules in chloroform solution; the transannular effect and position resistance may take place among molecules in LB films. These effects lead to the characteristic band at 686 nm, which is obviously enhanced and is explained by rare-earth metal bisphthalocyanine molecules existing mainly in associated species and the amount of monomers being considerably reduced in the LB film.

Fig. 5 shows how the absorbance value, measured at 686 nm, varies with the number of layers. The absorption increases linearly with the number of deposited layers. Though the molecule is not of the classical amphiphilic type, a straight line plot is obtained indicating reproducible quality, and the layers adhere tenaciously to substrates and to each other.

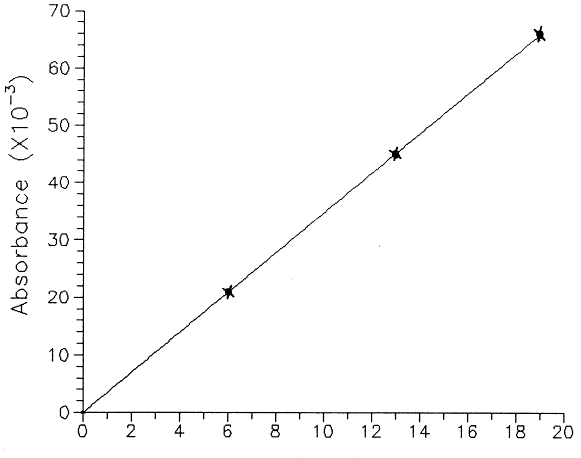

Fig. 5. Absorbance value, measured at 686 nm, vs. number of LB film layers.

3.3. Gas sensibility

For LB films without exposure to gases, a linear dependence of conductance on film thickness is obtained, which suggests that the conduction process is primarily a bulk phenomenon rather than a surface effect.

The response and recovery curves of the LB films of rare-earth metal bisphthalocyanine in different environments are shown in Figs. 6 and 7.

It is observed that:

(1) The conductance increases sharply with time at first when the sensor is made of Sm or Er bisphthalocyanine LB film contacting NO_2 gas. The conductivity increase is almost

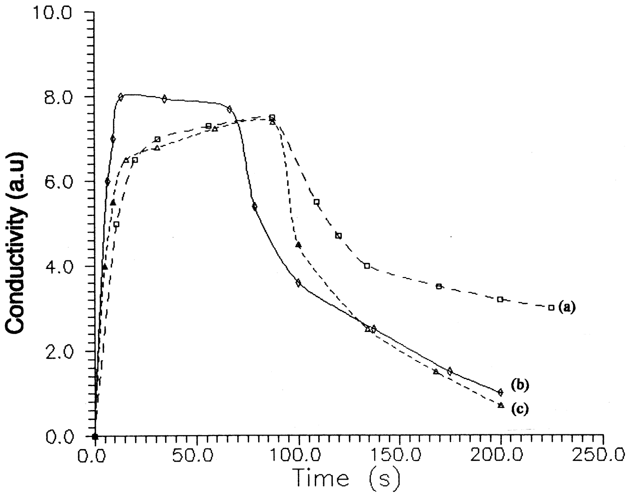

Fig. 6. Response and recovery curves of the LB films of rare-earth metal bisphthalocyanines in the vapor of 100 ppm NH_3: △, SmPc′$_2$; □, NdPc′$_2$; ◇, ErPc′$_2$.

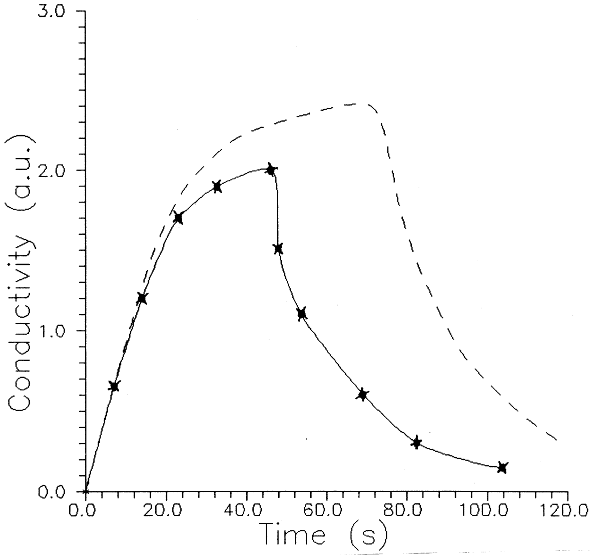

Fig. 7. Response and recovery curves of the LB films of rare-earth metal bisphthalocyanines in the vapor of 100 ppm NO_2: ——————, SmPc′$_2$; —∗—, ErPc′$_2$.

certainly the result of electrophilic attack of the extensive π-orbital system of the Pc molecule by the NO_2. The gas is chemisorbed on certain molecular sites and becomes negatively charged. This produces an increase in hole concentration and, hence, in the conductivity of the Pc molecule. The effect has been shown to be a surface phenomenon with kinetics governed by the Elovich rate equation, $d\theta/dt = a \exp(-b\theta)$ [12]. Then, the conductance increases slowly with time to the maximum response. The conduction process is a bulk phenomenon; the permeation of the gas to the bulk of the LB film appears to be necessary.

(2) When NO_2 gas is removed, the recovery also shows a rapid decrease, followed by a slower decrease of conductance. Active adsorption sites on the film surfaces are actually giving the fairly rapid initial recovery, and it is much more difficult for the gas to desorb in the bulk of the film.

(3) The irreversibility of NO_2 on bisphthalocyanine film (failure to return to baseline after NO_2 is removed) at indoor temperature may be attributed to its strong electronegativity and the bulk effect.

(4) The LB films of Sm and Er bisphthalocyanines have sensibility for vapors of NH_3 and NO_2, but the LB films of Nd bisphthalocyanine exhibit gas sensibility and selectivity only for the vapor of NH_3.

Chemisorption of a gas capable of inducing donor–acceptor interaction produces an ionized state and deforms the energy band structure. Metal phthalocyanines have two possible sites for gas adsorption: one is the central metal itself and the other is the π-electron system. The electrochemical oxidation of different phthalocyanines can therefore vary according to the metal used. It seems that the chemical properties of the two sites may change considerably and may in turn reflect the adsorption properties of the phthalocyanine towards oxidative gases.

Ammonia is electron donor gas, which usually reduces the conductivity of Pc films and crystals and readily reverses the effects of electron acceptor gases. The effect of ammonia on the electrical conductivity of substituted CuPc LB films has been explored [13,14]. Copper tetracumylphenoxy Pc and copper tetra-2,4-di-t-amylphenoxy Pc LB films show conductivity increases on exposure to NH_3. In this paper, when Sm, Er and Nd bisphthalocyanine LB films contact the NH_3, the conductance increases sharply with time at first, and then the conductance increases slowly with time to the maximum response. The possibility that may reflect cumulative chemisorption onto an n-type material conflicts with acceptor NO_2, and the mechanism leading to the conductivity increase in ammonia is not understood. Nd bisphthalocyanine LB films have no sensibility for the vapor of NO_2. It appears that the conduction phenomenon depends not only on the metal atom, but on the type of substituent as well.

4. Conclusions

The monolayer and deposition behaviors of rare-earth metal (Sm, Er and Nd) bisphthalocyanine derivatives ($LnPc'_2$) were studied. $LnPc'_2$ molecules existed mainly in associated species in LB films and the amount of monomolecules was considerably reduced. Though the $LnPc'_2$ molecule is not of the classical amphiphilic type, the absorption increased linearly with the number of deposited layers indicating reproducible quality and layers which adhered tenaciously to substrates and to each other. During the course of our work program on the characterization of phthalocyanine LB films, it was discovered that the conductivity of $LnPc'_2$ (Ln = Sm, Er) LB films was very sensitive to the presence of NO_2 and NH_3. In particular, the conductivity of $NdPc'_2$ LB films increased on exposure to NH_3 only. It appears that the conduction phenomenon depended on the central metal atom.

Further studies are needed to understand the mechanism leading to the conductivity increase in ammonia and to determine the gas sensing properties at higher temperatures.

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