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The Synthesis and Film-forming Property of a New Amphiphilic Phthalocyanine

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ABSTRACT

A new amphiphilic asymmetrical phthalocyanine has been synthesized and its film-forming property investigated by surface pressure–area isotherm and UV-visible absorption spectra. The oriented angle of the macroring was measured by polarized UV-visible absorption spectra, and the result coincided well with that deduced from the $\pi \sim A$ *isotherm. It is believed that the newly designed phthalocyanine can form a highly ordered Langmiur–Blodget film. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: phthalocyanine, LB film, polarized, UV-visible absorption spectra.

INTRODUCTION

Phthalocyanines are well known pigments which have some advantageous properties which render them important commercial commodities [1]. Robert and co-workers [2] were the first to demonstrate that phthalocyanines can be deposited as a thin film using the Langmuir–Blodget technique. The prospect of obtaining highly ordered films of phthalocyanines has pointed a new way forward for exploiting the interesting properties of phthalocyanines in sensors and electronic devices [3]. However, tetrasubstituted phthalocyanines are usually obtained as mixtures of isomers, which are likely to disrupt the highly ordered structure of the film. Octa-substituted phthalocyanines can be synthesized in an isomerrically pure form. We report here the synthesis of a

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novel amphiphilic phthalocyanine designed specifically for deposition as Langmuir–Blodget films, and its film-forming property.

EXPERIMENTAL

Synthesis

The target compound was synthesized by the route shown in Fig. 1

Preparation of 4,5-dibromocatechol (**2**)
Catechol (**1**) 17.8 g (0.15 mol) was suspended in 170 ml CCl_4 and cooled by salt-ice-water (−5°C). Br_2 64.2 g (0.4 mol) dissolved in 40 ml CCl_4 was dropped in for 1 h and the mixture stirred at room temperature for a further 16 h. The mixture was then filtered and white crystals obtained, 36.2 g yield 90% m.p: 120–122°C, MS ($C_6H_4O_2Br_2$): 268 (M^+).

Preparation of 1,2-dibromo-4,5-dipentyloxybenzene (**3**)
2 8.4 g (32 mmol) $C_5H_{11}Br$ 12.2 g (75.6 mmol) and anhydrous K_2CO_3 21 g was suspended in 80 ml DMF and was stirred at 80°C under a N_2 atmosphere for 5 h. The reaction mixture was cooled to room temperature, filtered and the residue washed with chloroform. The combined reaction solution and washings were evaporated to dryness, giving a wine colored residue, in which recrystallized from ethanol, as white needles (**3**) 11.0 g yield 85.4%. m.p.: 45–47°C, MS ($C_{16}H_{24}O_2Br_2$): 408 (M^+).

Preparation of 4,5-dipetyloxylphthalonitrile (**4**)
3 2 g (5 mmol) and CuCN 1.3 g (15 mmol) were refluxed in 24 ml dry DMF for 24 h. After cooling the reaction mixture to room temperature, it was poured into 70 ml 25% ammonia solution and stirred for 4 h. The mixture was filtered and the residue washed with water until the washings were colorless. A green solid was obtained, which was recrystallized from CH_3CN and purified by flash chromatography on silica gel using $CHCl_3$/petroleum ether (1:1, v/v) as eluent. The second fraction approved 0.55 g colourless crystals (**4**) yield: 37%. m.p.: 84–86°C MS ($C_{18}H_{24}O_2N_2$): 300 (M^+), IR (cm^{-1}): 3060, 2950, 2867, 2361, 1603.

Preparation of 3,6-di(2-hydoxyethanoxyl)phthalonitrile (**6**)
2-Iodoehtanol (15 ml, 21.2×10^{-2} mol), 2,3-dicyanohydroquinone (6 g, 3.7×10^{-2} mol) and anhydrous potassium carbonate 12 g in anhydrous acetone were heated under reflux for 60 h under a nitrogen atmosphere. The mixture was filtered while hot and the residue washed with warm acetone

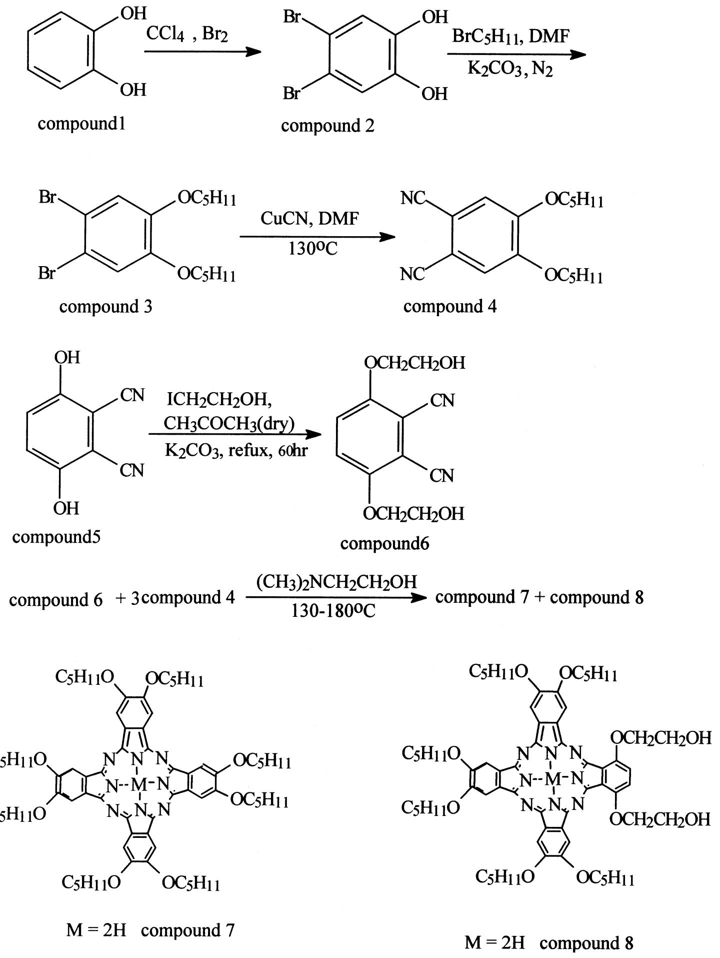

Fig. 1. Synthesis route of the phthalocyanines.

(4×80 ml). The washings were combined with the reaction liquor and the whole evaporated to dryness. The residue was washed with saturated $Na_2S_2O_3$ solution until the washings were colorless and then with water. Recrystallization of the crude product from acetone afforded 3,6-di(2-hydoxyethanoxyl)phthalonitrile (**6**) 5.22 g, yield 58%. m.p: 182.0–184.0°C. ^{1}H NMR (acetone- d_6): 3.18 (2H, s), 3.88 (4H, t), 4.25 (4H, t), 7.60 (2H, s). IR (KBr): 3300 cm^{-1} (–OH), 2250 cm^{-1} (CN). MS ($C_{12}H_{12}O_4N_2$) *m/z*: 248 (m^+).

Preparation of 2,3,9,10,16,17-hexapentyloxy-22,25-di(2- hydroxyethoxyl) phthalocyanine (**8**)

A solution of 200 mg (0.81 mmol) **6** and 2.25 g (7.3 mmol) of **4** in N,N-dimethylethanolamine (25 ml) were refluxed for 1 h at 130°C and the temperature was then raised to 180°C and maintained there for a further 12 h. After cooling to room temperature, 20 ml chloroform was added and the resulting solution was poured into 400 ml methanol and filtered. The resultant product was dissolved in a minimum amount of chloroform and purification was effected by chromatography on a silica gel GF_{254} column with dichloromethane as eluent. Residual solvent was removed under reduced pressure to give octapentyloxyphthalocyanine (**7**) 417 mg, MS ($C_{72}H_{98}O_8N_8$, m + 1): 1203. λ_{max} ($CHCl_3$,ε): 704 nm (1.21×10^5), 676 nm (1.02×10^5).

After elution of the first band $CH_2Cl_2/CHCl_3$(1:1, v/v) was then used as eluent and the next fraction contained the desired compound (**8**). The solution was evaporated to dryness in vacuum and 60.3 mg dark green product was obtained, yield 6.5%. λ_{max} ($CHCl_3$,ε): 710 nm (1.12×10^5), 690 nm (1.15×10^5). MS ($C_{66}H_{88}O_{10}N_8$) *m/z*: 1151 (m + 1).

Monolayer and LB film deposition

Surface pressure–area isotherms and the film deposition were carried out using a JDLB 2000 model LB balance (Jilin Uiniversity, Changchun, China) at 19–21°C. The monolayer was spread onto a water subpase from a solution of the target compound **8** (5.6×10^{-4} mol liter^{-1}) in chloroform. The multilayer were prepared on a glass substrate which had been cleaned by supersonic treatment with chloroform, acetone and pure water for 15 min successively before use. The surface pressure was kept constant at 55 and 38 mN m^{-1} respectively, resulting in fairly good deposition of typical Y-type film.

Instrumentation

UV-visible absorption and polarized absorption spectra were measured on a Hitachi 557 UV-visible spectrometer. Mass spectra was performed on a VGTRIO-2000 and VG platform II ESI. IR spectra were recorded on a Hitachi 983G spectrometer.

RESULTS AND DISCUSSION

Surface pressure–area isotherm

Figure 2 shows the surface pressure–area isotherm at 21°C for the monolayer of compound **8** and with compound **7** for comparison, spread from chloroform solution onto the water surface. There is a distinct phase transition and

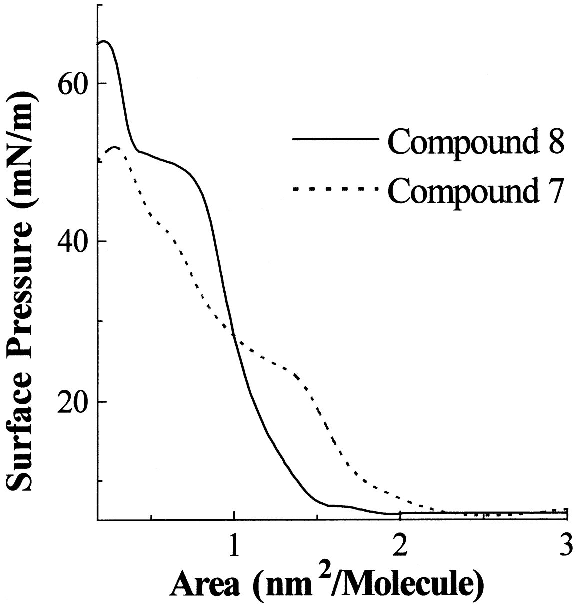

Fig. 2. $\pi - A$ isotherms for the monolayers of compound **7** (...) compound **8** (—) at 19–21°C.

two abrupt increases in slope, with a plateau, indicating that two kinds of well-condensed monolayers are formed. The area per molecule of the film was estimated to be 1.24 nm^2 before the plateau. From the CPK molecular model, compound **8** occupies a minimum area of about 3.04 nm^2 per molecule in a plane. We can calculate that the macroring of compound **8** is inclined to the water surface at an angle of 66° when the pressure was kept below the plateau. After that a second abrupt increase of slope occurred. If the second linear portion of the isotherm is extrapolated to zero surface pressure, the intercept gives the area per molecule to be 0.76 nm^2, indicating that the macrorings of compound **8** reorientated themselves to a more closely packed manner, and stand nearly perpendicular to the water surface. A completely different type of isotherm is observed for compound **7**; there is no distinct phase transition and the area per molecule remain at values much higher than those for close packing. This type of film is known to be highly expanded and less stable. Thus we can see clearly that the introduction of two hydroxy groups distinctly improved the film-forming property of phthalocyanine.

LB film deposition

The monolayer of compound **8** was transfered to the substrate by the vertical-lifting method at 55 mN m^{-1}, with a transfer ratio of 0.8–1.0 and a Y-type film was obtained. Figure 3 shows the UV-visible absorption spectra of multilayers of the LB films compared with solution spectra; the inset is the plot of absorbance at 660 and 650 nm vs the number of layers. In the film spectra, the Q band at 690 nm and 710 nm are broadened, indicating the occurrence of molecular aggregation of compound **8** in the film. Plot of the absorbance of a band at 660 nm of the deposited film vs the number of layers results in a straight line, as shown in the inset of Fig. 3, indicating a fairly constant transfer ratio during sequential dipping of the slide through the film and uniform deposition. The film deposited at 38 mN m^{-1} showed the same result.

Dichroism

For evaluation of the orientation of the phthalocyanine ring in LB film, polarized UV-VIS spectoscopy was used, and the dichroic ratio D and biaxial orientation parameters calculated according to the Yoneyama equation [4] are listed in Table 1.

The orientation angle of the macroring with respect to the substrate was calculated to be 67° and 87° at surface pressure of 38 and 55 mN m^{-1} respectively, which are well coincident with the result deduced from the surface pressure–area isotherm. It is apparent that at lower surface pressure the macroring was somewhat tilted from the substrate and was oriented nearly

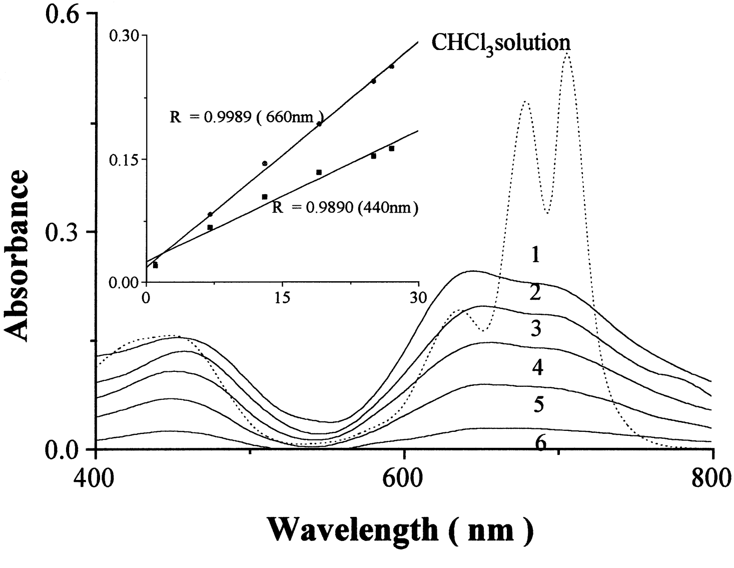

Fig. 3. Absorption spectrum of the mulitlayers compared with the solution spectra (1, 27 layers per side; 2, 25 layers per side; 3, 19 layers per side; 4, 13 layers per side 5, 7 layers per side; 6, 1 layers per side. Inset is the plot of the absorbance vs the number of layer).

TABLE 1
Result of Polarized UV-vis Absorption Spectroscopy.

Type of LB film		π =38 mN m^{-1}	π =55 mN M^{-1}
$\beta' = 0°$	$A_{//}$	0.087	0.139
	$A_{\perp}$	0.054	0.110
	D_0	1.611	1.264
$\beta' = 45°$	$A_{//}$	0.090	0.117
	$A_{\perp}$	0.073	0.131
	$D_{\beta'}$	1.236	0.895
$\cos^2\theta$		0.139	0.003
θ		67°	87°

perpendicular to the substrate when the surface pressure was higher. There was no apparent change in the orientation of the molecule when the monolayer was transfered from the water subphase to the substrate. In both cases significant anisotropy existed in the layer plane.

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