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The synthesis of asymmetrically substituted amphiphilic phthalocyanines and their gas-sensing properties

Ximing Ding, Shuying Shen, Qingfu Zhou, Huijun Xu *

Institute of Photographic Chemistry, Academia Sinica, Beijing, 100101, People's Republic of China

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Abstract

A series of asymmetrically substituted amphiphilic phthalocyanines have been synthesized. They have been deposited as Langmuir–Blodgett films onto glass and/or glass substrates bearing aluminum interdigitated electrode patterns. The films show fast response to NO_2 with almost complete recovery at room temperature. It is indicated that layer ordering and molecular packing within the LB films are important factors determined the gas-sensing properties.

Keywords: Phthalocyanine; LB film; Gas-sensor; NO_2

1. Introduction

Phthalocyanines are excellent pigments and p-type semiconductors. The observation that the semiconducting properties of phthalocyanines are modulated by the adsorption and desorption of gases led to significant efforts toward their incorporation as thin films in gas-sensors [1]. For the preparation of thin films of phthalocyanines the Langmuir–Blodgett technique has been shown to be advantagous in depositing controlled thickness and highly ordered structures over solid substrates and interdigital electrode arrays in order to manufacture small vapor detectors. In turn, this has led to a quest for derivatives with properties suited for the LB technique. Most research work has been centered on phthalocyanines bearing four substitutent groups. However, tetra-substituted derivatives are usually obtained as a mixture of isomers, which are likely disrupt the highly ordered structure of the films. Octa-substituted phthalocyanines can, however, be synthesized isomerically pure. Furthermore, introduction of amphiphilic character encourages molecular ordering [2]. Using a related phthalocyanine substituted with six alkyl-groups and two hydrophilic tails, well-ordered film formation as well as useful room temperature response to NO_2 has been shown [3], but as yet, incomplete recovery characteristics remain to be improved.

Previously, we reported the synthesis and film-forming properties of an example of the series of asymmetrically substituted phthalocyanine as shown in Fig. 1 [4]. The present paper reports the synthesis of the other two compounds of the series and the response of these compounds to NO_2. The results show that in each case, the response is fast

* Corresponding author. Tel.: +86-10-6488-8176; Fax: +86-10-6202-9375.

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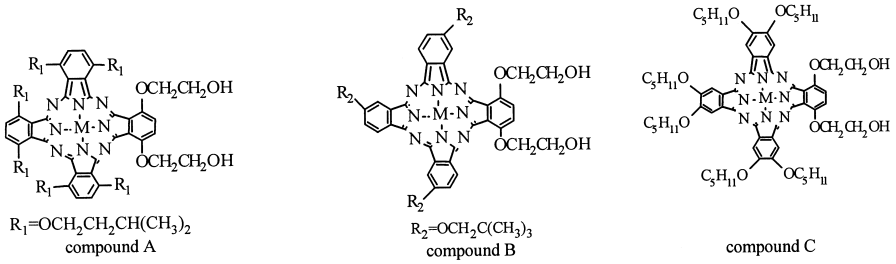

Fig. 1. The structure of the title compounds.

with almost complete recovery, and layer-ordering and molecular packing within the LB films are important factors determining the gas-sensing properties.

2. Experimental

2.1. The synthesis of the compounds

Fig. 1 gives the structure of the title compounds. The synthesis of compound C has been reported elsewhere [4].

2.1.1. 1,4-diisopentyloxyphthalonitrile (1)

2,3-dicyanohydroquinone (1 g, 6.25 mmol), isopentyloxyl bromide (2.2 g, 13.8 mmol) and anhydrous potassium carbonate (2 g) were suspended in 40 ml dry DMF and heated at 90°C in an N_2 atmosphere for 12 h. The reaction mixture was cooled to room temperature and poured into 200 ml water. The precipitate was filtered and washed with water until the washings became neutral; 1.33 g of white crystals were obtained, yield 71%, m.p.: 212–213°C ^{1}H NMR ($CDCl_3$): 7.55 (s, 2 H), 4.22 (t, 4 H), 1.70 (m, 4 H), 0.95 (m, 7 H), IR (KBr): 2250 cm^{-1}(s, CN). MS for $C_{18}H_{24}O_2N_2$ m/z: 300(m^+).

2.1.2. 1,4-dihydroxyethoxy-8,11,15,18,22,25-hexaisopentyloxyphthalocyanine (A)

1 (150 mg, 0.5 mmol) and 3,6-di(2-hydoxyethoxyl)phthalonitrile **2** (prepared according to the literature method [4]) (40 mg, 0.16 mmol) in dry pentan-1-ol (5 ml) were heated to reflux in an N_2 atmosphere, and lithium metal (90 mg) was then added portionwise. Refluxing was continued for 1 h and the mixture was then allowed to cool to room temperature; the mixture had a dull olive color. When glacial acetic acid (20 ml) was added, stirring for 1 h, the mixture became wine color. The solvent was removed under reduced pressure and the residue taken up in chloroform (20 ml) and washed with saturated sodium carbonate solution and water until the washings were neutral. The green solution was then dried with anhydrous $MgSO_4$, filtered and chloroform removed under reduced pressure giving a dark green viscous oil. It was chromatographed over silica gel column (GF_{254}) using a mixture of light petroleum (60–90°C)–THF 9:1 as eluent, giving, as a green solid, 1,4,8,11,15,18,22, 25-octaisopentyloxylphthalocyanine (58 mg); UV-VIS (toluene) $\lambda(\log\epsilon)$: 760 nm (5.17), 730 (5.08); MS(ESI) for $C_{72}H_{98}O_8N_8$ m/z:1203 (m + 1). On increasing the polarity of the eluent (petroleum–THF 4:1), a second fraction, viz. 1,4-dihydroxyethanoxyl-8,11, 15,18,22,25-hexaisopentyloxyl phthalocyanine (**A**) was obtained (10.5 mg yield 5%); UV-VIS (toluene) $\lambda(\log\epsilon)$:758 nm (5.21), 726 (5.14). MS(ESI) for $C_{66}H_{86}O_{10}N_8$ m/z: 1151 ($m^+ + 1$).

2.1.3. 1,4-dihydroxyethoxy-9,16,23-trineopentyloxyphthalocyanine (B)

2 40 mg (0.16 mmol), 4-neopentyloxylphthalonirile **3** (synthesized according to the literature [5]) 310 mg (1.14 mmol) and 5 ml ethanolamine were refluxed for 1 h under NH_3 and the temperature was then raised to 180°C and maintained for another 10 h. The liquor was cooled to room temperature, dissolved using a minimum amount of chloroform, and the solution poured into 200 ml methanol. It was filtered giving a dark green solid, which was purified on a silica gel column (GF_{254})

using dichloromethane as eluent, giving as first fraction 2,9,16,23-tetraneoprntyloxylphthalocyanine (78 mg); UV-VIS/$CHCl_3$ (λ, logϵ): 676 nm (5.18), 660 nm (5.09). MS(ESI) for $C_{52}H_{58}O_4N_8$ m/z: 859 ($m^+ + 1$). Then using CH_2Cl_2:$CHCl_3$ (1:1) as further eluent, the second fraction, compound **B** was obtained, (9.5 mg, yield 6.6%) MS(ESI) for $C_{51}H_{56}O_7N_8$ m/z: 893 (m + 1), UV-VIS/$CHCl_3$ (λ, logϵ): 704 nm (5.26), 688 (5.22).

2.2. Monolayer and LB film fabrication

The monolayers were spread from chloroform solution (5.6×10^{-4} mol/liter) onto double-distilled water (pH = 5.6). A KSV-5000 twin-compartment LB trough was used for the measurements of surface pressure-area (π-A) isotherm and the preparation of the LB films. The LB films were built up on glass substrates and/or on glass with aluminum interdigital electrodes for spectroscopic studies and conductance measurements, respectively. A constant surface pressure of 26 mN/m for **A**, 36 mN/m for **B** and 38 mN/m for **C** was maintained, resulting in fairly good deposition of typical Y-type films. UV-VIS absorption spectra were measured using a Hitachi 557 spectrophotometer.

2.3. Conductance measurement

The lateral conductance of the LB films and dynamic gas-sensing response characteristic were monitored using a current-voltage (I-V) measuring apparatus composed of a DH1718DC power supply, a microvolt amplifier and an LZ3-100 X-Y function recorder, linked with a Teflon and glass gas-testing system consisting of inlets and flowmeters for introduction of gases, a mixing chamber and a testing chamber [6].

3. Results and discussion

3.1. Monolayer behavior and LB film deposition

Materials were tested for their suitability for solid film preparation utilizing the LB technique. The monolayer were prepared on a water surface and successfully transferred onto glass slides. Fig. 2 shows the surface pressure-area isotherms at 21°C for the monolayers of compound **A**, **B** and **C**. In the π-A isotherm of compound **C** (curve 3) there is distinct phase transition and two abrupt increases in slope and exhibiting a plateau, indicating that two kinds of well-condensed monolayers had been formed. The lower pressure region corresponds to monolayer and the higher pressure region corresponds to bilayer. Compound **B** gives slightly different π-A isotherm (curve 2) without a plateau. Compound **A** shows somewhat expanded π-A isotherm (curve 1) and it can be seen that the monolayer collapses at a relatively low pressure compared with curves 2 and 3, suggesting that the monolayer is less stable.

These monolayers can be transferred onto glass substrates by the vertical lifting method to form a Y-type film. Fig. 3 gives the UV-VIS absorption spectra for the multilayers of the titled compounds compared with each solution spectrum. In the film spectra of **A** the absorption peak appears at ca. 775 nm, which is broadened and red-shifted relative to the band position in solution, consistent with non-fully cofacially aligned stacking of molecules within a columnar assembly. The film spectra of **B** and **C** shows that in each case the absorption band is broadened and blue shifted

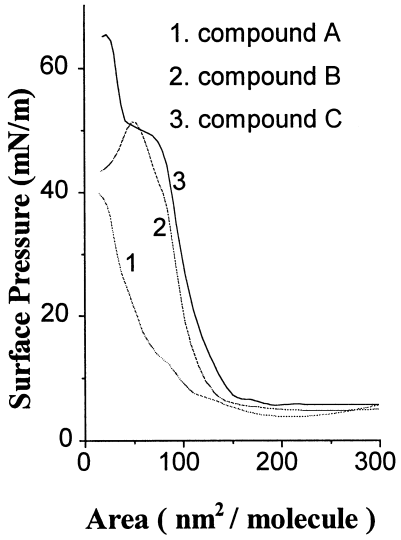

Fig. 2. Surface pressure-area isotherm of title compounds at 21°C.

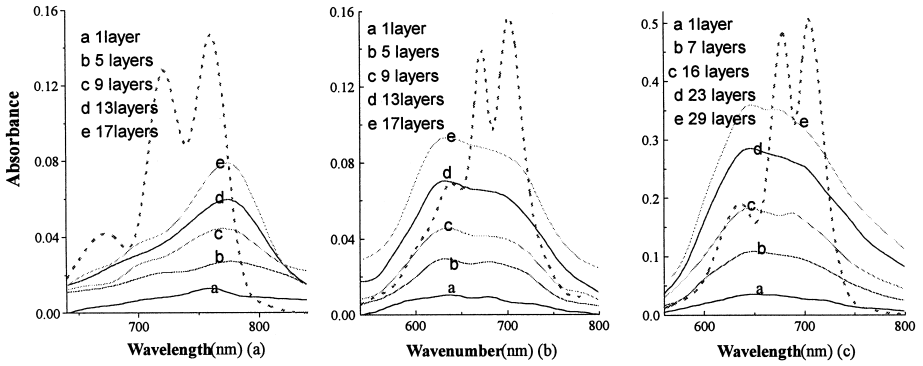

Fig. 3. Absorption spectra of 1(A), 2(B), 3(C) LB films (solid lines) of different number of layers compared with their solution spectra (dot line).

compared with solution spectrum attributed to cofacial columnar structure.

3.2. Gas-sensing properties of the LB films

The gas-sensing properties of the LB films of the three compounds to different concentrations of NO_2 were determined. Fig. 4 shows the response and recovery process of the LB films to NO_2, in which t_a refers to the time needed for adsorption of NO_2 to saturation, t_d refers to the time needed for desorption of NO_2.

Table 1 gives the response and recovery characterics of 9-layer LB films of the compounds to NO_2. Comparison of the data for the three compounds shows that the magnitude of the initial conductance of the films of compound **C** is 3 to 10 times larger than that of **A** and **B**. The response speed is in the order: **C** > **B** > **A**. The response of compound **C** is particularly rapid and strong compared with **A** and **B**, and increases with increasing NO_2 concentration. This may be attributed to the difference in structure and molecular packing of the molecules in different films. Low angle X-ray diffraction studies of LB films of compound **C** showed a Bragg peak at $d = 4.1$ nm (X. Ding, unpublished results), consistent with a well-ordered bilayer structure, and the macroring of the molecules are not lying flat on the substrate surface but rather subtend to a certain angle to the surface with molecular plane of the molecules arranged cofacially. Neither film of compound **A** and **B** gave any Bragg peaks, suggesting little or no layer ordering, leading to weaker and slower response.

To investigate the reversibility of the gas-sensing properties, the films were exposed to NO_2 repeatedly. Each cycle of exposure lasted for 3 min

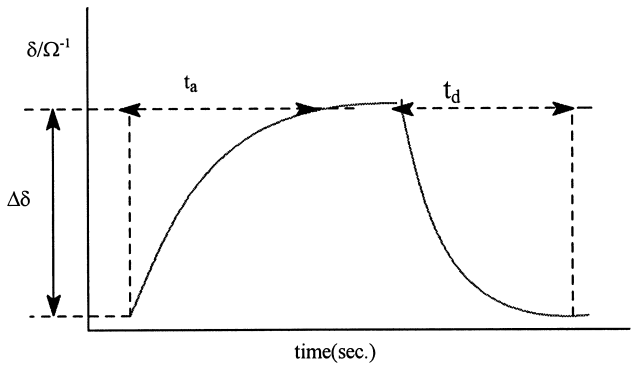

Fig. 4. The response and recovery process of phthalocyanine LB fims to NO_2.

Table 1
The response characteristic of 9-Layer LB films of the title compounds to NO_2

Compound	δ_0 ($10^{-9}\,\Omega^{-1}$)	Gas	Gas concentration (ppm)	t_a/s	t_r/s	t_d/s	$\Delta\delta$ ($10^{-9}\,\Omega^{-1}$)
A	0.26	NO_2	20	33	25	37	0.32
B	0.85	NO_2	20	39	34	45	0.92
C	2.58	NO_2	20	7	4	135	21.05
			10	9	5	148	10.75
			1	40	33	166	6.37

t_r is the response time defined as the time after a 75% change in the stationary signal; δ_0 is the film conductance in air.

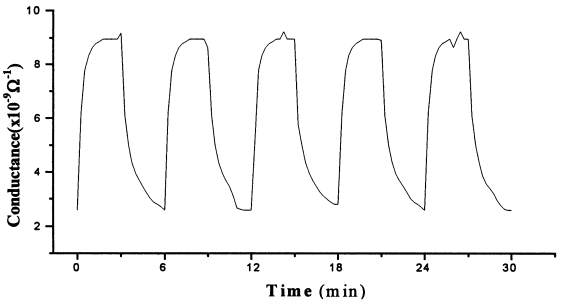

Fig. 5. The response cycles of 9-layer LB films of C deposited at 35 mN/m to 1 ppm NO_2.

followed by recovery in air for 3 min. In each case, good reversibility at room temperature was observed. We take the response of the films of compound **C** to 1 ppm NO_2 as an example, as indicated in Fig. 5.

4. Conclusion

Asymmetrically substituted amphiphilic phthalocyanines show fast response to NO_2 with almost complete recovery at room temperature. The response behavior is influenced by both the chemical and physical structure of the films. The response speed follows the order: compound **C** > compound **B** > compound **A**. Compound **C**, which formed highly ordered films with molecular planes of the phthalocyanines face to face with each other, is superior to the others for gas-sensing application.

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