The anisotropic gas response behavior of LB films of an amphiphilic asymmetrically substituted phthalocyanine

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Abstract

1,4-Di(2-hydroxyethoxy)-9,10,16,17,23,24-hexapentyloxy phthalocyanine (asy-Pc) has been deposited as well-ordered Langmuir–Blodgett (LB) films on a glass substrate and glass-bearing interdigital electrodes. The molecular orientation of the asy-Pc LB films has been characterized by polarized UV-vis absorption spectra and in-plane dichroism has been observed. The LB films show good room temperature response to NO_2 gas and the recovery is almost complete. It has been found that the magnitude of the response increases with increasing gas concentration and is also dependent upon the LB dipping direction relative to the arms of the electrodes, consistent with conduction being favored along the axes of the stacks of asy-Pc molecules. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

The semiconductivity of phthalocyanine (Pc) films is strongly affected in the presence of adsorbed electron–acceptor gases, a property which has potential for application in gas-sensing devices [1]. The response and recovery of gas-sensing devices based on sublimed Pc films are generally slow. Performance is better at elevated temperature and film morphology, i.e. crystalline size and orientation plays an important role in the film conductance and gas-sensing properties [2]. It is believed that film morphology must accommodate both the charge transfer interaction and carrier transport. Using Langmuir–Blodgett films by introducing appropriate substituents into the phthalocyanine macro-ring, the molecular orientation and stacking of the molecules in the films could be controlled. Their electrical properties may be tuned and improved. Previously, we reported the synthesis and film-forming properties of a novel amphiphilic octa-substituted phthalocyanine depicted in Fig. 1 [3]. This compound can be deposited as well-ordered LB films. The observation of in-plane dichroism indicated the presence of some degree of anisotropic order of molecules whose planes are tilted to the substrates. The present paper reports the molecular orientation and gas response behavior to NO_2 of novel Pc LB films with differ-ent dipping direction relative to the arms of the electrodes. The observed anisotropic response is attributed to the structural anisotropy.

2. Experimental

The synthesis of the amphiphilic octa-substituted phthalocyanine, 1,4-di(hydroxythoxy)-9,10,16,17,23,24-hexapentyenlocy phthalocyanine (asy-Pc) was reported elsewhere [3]. A KSV-5000 twin-compartment LB instrument was used for the fabrication of the LB films. The monolayers were spread from chloroform solution on deionized water (with resistivity greater than 18 MΩ/cm,
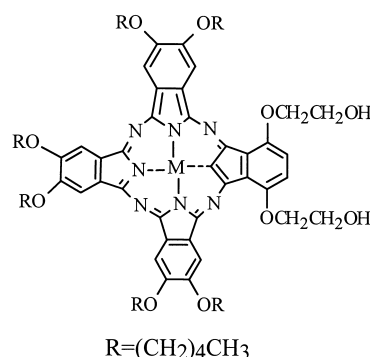

Fig. 1. Structure of the amphiphilic phthalocyanine.

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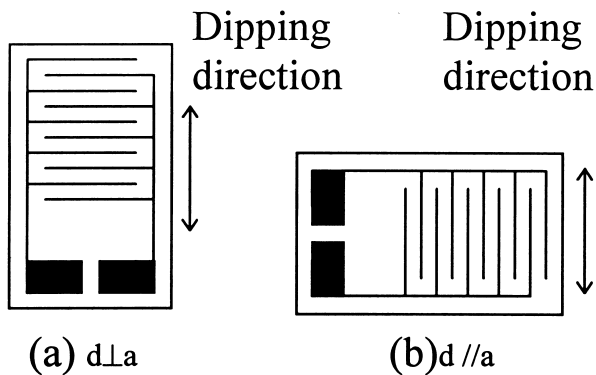e-mail: g201@ipc.ac.cn.

Fig. 2. Schematic diagram of substrates dipped to prepare LB films. (a) Dipped perpendicular to the arms of the electrodes, (b) dipped parallel to the arms of the electrodes.

pH ≅ 5.0). The asy-Pc LB films were prepared on glass substrate and on glass bearing interdigital aluminum electrodes consisting of 50 finger pairs of electrodes with a width of 50 μm and a gap-width of 50 μm. Dipping was vertical at a speed of 5 mm/min and at a constant surface pressure of 38 mN/m, resulting in remarkable Y-type deposition with a transfer ratio of 0.8–1.0. One set of substrates was dipped such that the dipping direction, d,

Table 1
Polarized UV-vis spectra data

$\beta' = 0°$	$A_{\parallel}$	0.087
	$A \perp$	0.054
	D_0	1.611
$\beta' = 45°$	$A_{\parallel}$	0.090
	$A \perp$	0.073
	$D\beta$	1.236
$\cos^2\theta$		0.1390
θ		67°
ϑ		35°

was perpendicular to the arms, a, of the electrode, $(d \perp a)$, and a second set such that d was parallel to a, $(d \parallel a)$, as shown in Fig. 2.

UV-visible absorption spectra were measured on a Hitachi 557 UV-visible spectrometer. The conductance and dynamic gas response characteristic of the LB films were monitored using a current–voltage (I–V) measuring apparatus linked with a Teflon and glass testing system consisting of inlets and flow meters for the introduction of gas, a mixing chamber and a testing chamber as described previously [4]. All the experiments were carried out at room temperature.

3. Results and discussion:

3.1. Molecular orientation of LB films

For evaluation of the orientation of the phthalocyanine ring in the LB films, polarized UV-vis spectroscopy is used and the dichromic ratio D and biaxial orientation parameters are calculated according to the Yoneyama equation [5]

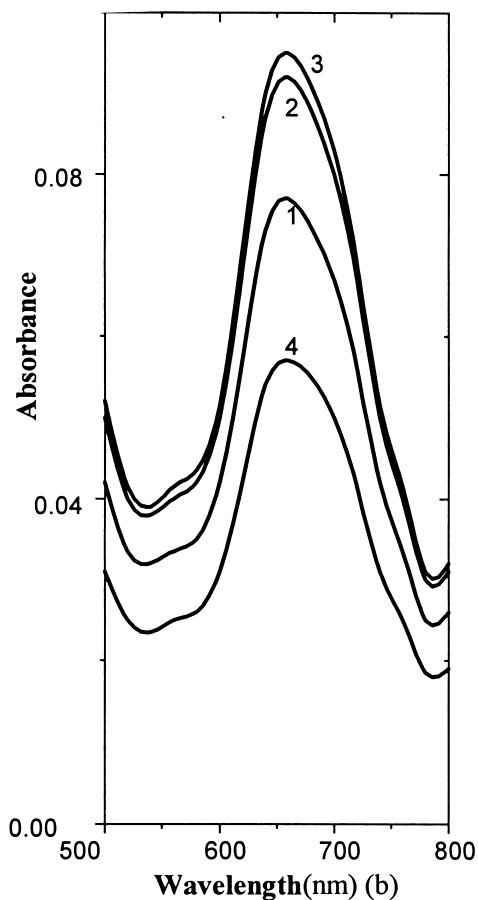$$\cos^2\theta = \frac{D_0 - \left(1 + D_0\sin^2\beta\right)D_\beta}{(1 - 2\sin^2\beta)D_\beta - \left(1 + D_\beta\sin^2\beta\right)D_0}$$

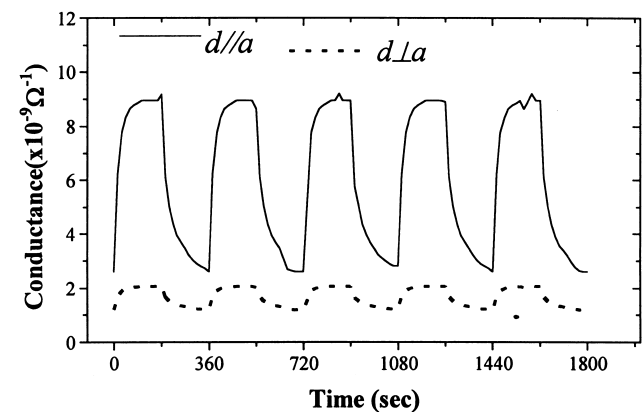Fig. 3. Polarized electronic spectra of the LB films (five layers) (1 ⊥ 45°; 2 ∥ 0°; 3 ∥ 45°; 4 ⊥ 0°).

Fig. 4. The response and recovery of nine-layer asy-Pc LB films deposited with two different dipping directions as sequential exposure to 1 ppm NO₂.

Table 2
The gas-sensing parameters of the two kinds of LB films to NO_2 gas

Dip direction	$\delta(\times 10^{-9}\ \Omega^{-1})$	Gas concentration (ppm)	t_a	t_r (s)	t_d (s)	$\Delta\delta\ (\times 10^{-9}\ \Omega^{-1})$
$d \perp a$	1.18	20	6	4	120	4.02
		2	30	26	156	1.56
		1	44	37	172	0.87
$d \perp a$	2.58	20	7	4	135	21.05
		10	9	5	148	10.75
		1	40	33	166	6.37

$$\sin^2\theta\cos^2\phi = \frac{D_0 - \cos^2\theta}{1 + D_0}$$

where $\beta = \sin^{-1}(n_1\sin\beta'/n_2)$, n_1 and n_2 are the refractive index of air and the film, respectively, here $n_1 = 1$ and $n_2 = 1.23$, β' is the incident angle, D_0 and $D\beta$ are the dichronic ratio for the $\beta = 0°$ and $45°$, respectively and to be defined as $A_\parallel/A_\perp$, θ is the orientation angle between the molecular axis of the phthalocyanine macro-rings and the normal of the substrate plane with an azimuth of ϕ in the substrate plane.

The polarized absorption spectra of asy-Pc LB films are illustrated in Fig. 3. The observation of dichroism indicates an anisotropic arrangement of the molecules in the films. The greater absorption observed when the electric field vector of the incident radiation E is parallel to the dipping direction is consistent with the fact that the phthalocyanine macro-rings are orientated nearly perpendicular to the substrate surface. Table 1 gives the polarized UV-vis spectroscopic data for five layers asy-Pc LB films. The results indicate that the phthalocyanine macro-rings are tilted with an angle of $67°$ to the substrate with molecular planes of phthalocyanine face-to-face with each other with an azimuth $\varphi = 35°$ indicating that when $d \parallel a$ the stacks are aligned preferentially along the shortest distance between the electrodes and the stacks are aligned along a longer path when $d \perp a$.

3.2. Gas-sensing properties

The asy-Pc LB films deposited with two dipping directions were exposed to NO_2 gas for 3 min followed by recovery in clean air for another 3 min repeatedly at room temperature. Fig. 4 shows the response and recovery of nine-layer asy-Pc LB films deposited with two different directions as sequential exposure to 1 ppm NO_2. They give fast and strong response at room temperature with almost complete recovery. Table 2 shows the gas-sensing parameters of the two films on exposure to different NO_2 concentration, where t_a refers to the time needed for the adsorption process, t_r is the response time which is defined as the time required for 75% of the stationary conductance value, t_d is the recovery time corresponding to the desorption process, δ_0 is the conductance of the LB film in dry air, $\Delta\delta$ is the conductance change of the LB films before and after exposure to NO_2. It can be seen from Table 2 that the higher the gas concentration, the stronger the response signal $\Delta\delta$ and the shorter the response (t_r) and the recovery(t_d) time. Fig. 4 shows that the recovery is nearly complete. There is no significant difference between the two kinds of LB films for the response and recovery time, indicating that the two films follow the same adsorption and desorption kinetics. Whereas the initial conductance (δ_0) is larger by a factor of about 2 for the film of $d \parallel a$, and the response signal ($\Delta\delta$) is about 4–6 times larger than that of $d \perp a$, consistent with conduction being favored along the stacking direction, which is ascribed to a greater mobility of carriers transported through π-orbitals between adjacent phthalocyanine molecules.

4. Conclusion

1,4-Di(2-hydroxyethoxy)-9,10,16,17,23,24-hexapentyloxyphthalocyanine can be deposited as well-ordered Langmuir–Blodgett films. The results of polarized absorption spectra indicate that the phthalocyanine macro-rings are tilted with an angle of $67°$ to the substrate surface with the planes face-to-face with each other. In-plane dichroism was observed. The anisotropic gas response behavior is attributed to structural anisotropy.

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