JOURNAL OF
Materials
CHEMISTRY

Novel crown ether substituted phthalocyanine with good gas sensing properties to NO_2

Xiyou Li,*[a]† Yanli Chen[b] and Huijun Xu[c]

[a]*Department of Chemistry, Shandong Teachers' University, Jinan 250014, China*
[b]*Department of Chemistry, Jinan United University, Jinan 250002, China*
[c]*Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China*

Received 10th March 1999, Accepted 30th March 1999

A novel 18-crown-6 substituted phthalocyanine was synthesized. LB films of this material were prepared by a vertical dipping method and the structures of the films were characterized by absorption spectra, polarized absorption spectra and X-ray diffraction experiments. The results indicate that the films possess highly ordered structures. The LB films display good gas sensing properties to NO_2 with a high sensitivity, quick response and good reversibility at room temperature.

Introduction

As functional materials, phthalocyanine and many of its derivatives exhibit properties which are interesting for applications in many fields such as optical storage, electrochromic displays, electrophotography, photovoltaic cells and gas sensing devices.[1] The study of phthalocyanines as gas sensing materials has been an active area of research over several decades.[2,3] The principles and the mechanisms of gas response[4,5] have been studied. Sublimed,[6] cast[7] and Langmuir–Blodgett (LB) films[8] of phthalocyanines are used in the studies of the gas sensing properties. Crown ether substituted phthalocyanines are newly developed members of the phthalocyanine family. They have been prepared by several groups[9–11] and it was found that alkali ions with an appropriate diameter can induce their aggregation.[12,13] Wright and coworkers discovered that cast films of tetra-crown ether substituted phthalocyanines display very good gas sensing properties with high sensitivity, quick response and good reversibility at room temperature.[7,14] This is the first example of phthalocyanine films that display quick response and good reversibility at room temperature.

The orderless structure and the difficulty in controlling the thickness precisely[7] of the cast film which was used by Wright in his research work are the main defects of this kind of material. The high sensitivity to humidity is also an obstruction to practical applications. For the purpose of fabricating crown ether substituted phthalocyanines into highly ordered LB films and reducing the sensitivity to humidity we have introduced three hydrophobic alkyl chains into the phthalocyanine ring and prepared a series of mono-crown ether substituted phthalocyanines. These phthalocyanine analogues containing hydrophilic crown ether rings and hydrophobic alkyl chains are amphiphilic and suitable for fabricating into LB films.[15] We have studied the LB films and the gas sensing properties of mono 15-crown-5 substituted phthalocyanines.[16] The results indicate that this kind of material can form very stable LB films with a very ordered and compact structure. The LB films display a very slow response and reversible process while the corresponding spin coated films display a quick response and good reversibility at room temperature. This indicates that the structure of the film determines the gas sensing properties. The slow response and reversal process may be ascribed to the compact structure which slows down the diffusion of NO_2 molecules in the film. For the purpose of fabricating phthalocyanine into an ordered but loosely packed structure, 18-crown-6 (with a bigger bulk than that of 15-crown-5) was introduced into the phthalocyanine ring (**1**) (Fig. 1a). The minimized molecular structure of the 18-crown-6 substituted phthalocyanine (Fig. 1b) shows that the ring of 18-crown-6 in the molecule bends to one side of the phthalocyanine ring. This conformation hinders the molecules of phthalocyanine from arranging tightly. A large space may be left in the film. The structures and the gas sensing properties of this kind of LB film have been studied. Here we report the results.

Results and discussion

The film forming properties

Fig. 2 shows the π-A isotherms of **1** on a water surface. It indicates that the compound can form a very stable monolayer on a water surface with a collapse surface pressure of $40\ \mathrm{mN\ m^{-1}}$. The monolayer can be transferred to substrates freely by a vertical dipping method to form Y type LB films (average transfer ratios are 0.85 and 0.92 for down and up strokes respectively). The transfer processes were monitored by the absorption spectra of the films (Fig. 3). The linear relationship between the layer number and the absorbance (inset of Fig. 3) at the absorption peak (650 nm) indicates that the transfer is complete and stable.

The molecules of phthalocyanines always form aggregates (face to face) in LB films and give a broad absorption peak at 620–630 nm.[16] The absorption spectra of compound **1** display a peak at 650 nm; there is a red shift of about 20 nm compared with that of the aggregate and a blue shift of about 15 nm compared with that of **1** in solution (two peaks, at 665 and 705 nm respectively). The π-A isotherms of **1** on a water surface also tell us that the mean molecular area of **1** is bigger than that of mono 15-C-5 substituted phthalocyanines.[17] These results indicate that compound **1** forms a loosely arranged LB film with a relatively big space between phthalocyanine molecules.

Fig. 4 gives the polarized absorption spectra of the LB films of **1**. The big differences between the absorbances in response to different polarized light indicated that the films are highly ordered. The orientations of the molecules of **1** in the film were calculated by the method of Yoneyama.[18] The results (Table 1) indicate that the molecules of **1** are inclined to the surface of the substrate at an angle of 55°.

The X-ray diffraction pattern (Fig. 5) gives two peaks ascribed to the first and the second grade diffraction respect-

---

† *Present address*: Chemistry Department, Chinese University of Hong Kong, Shatin N. T. Hong Kong, China.
E-mail: b101009@mailserv.cuhk.edu.hk

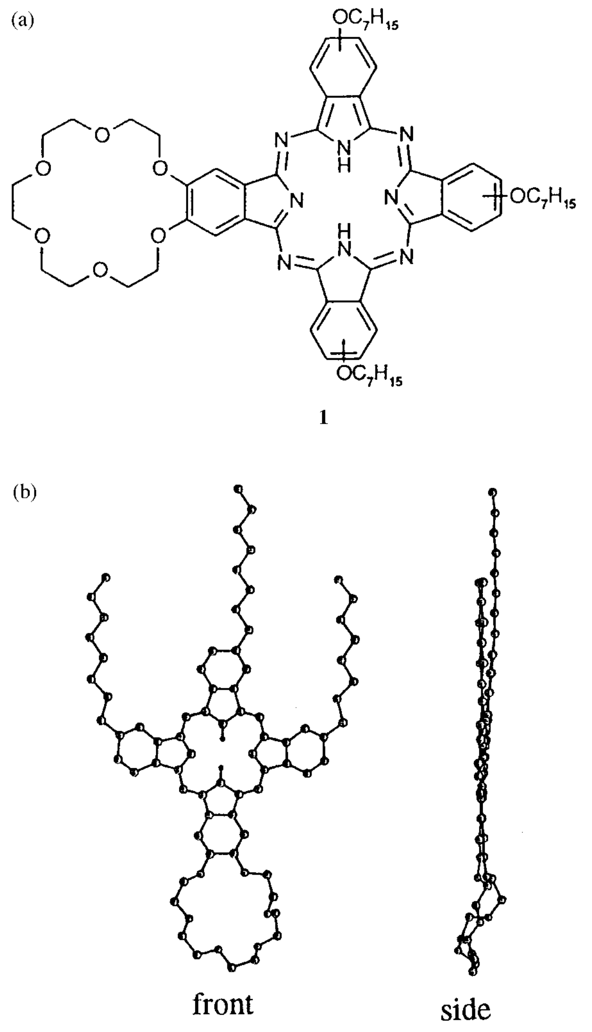


Fig. 1 Structure of the 18-crown-6 substituted phthalocyanine (a) and the minimized molecular structure (b).

ively. This indicates that the film possesses good layer structures. The layer thickness of the film calculated from the value of θ is 2.2 nm. It is smaller than the diameter of the molecule calculated from a molecular model. So we estimate that the hydrophobic chains of **1** in different layers may overlap each other.

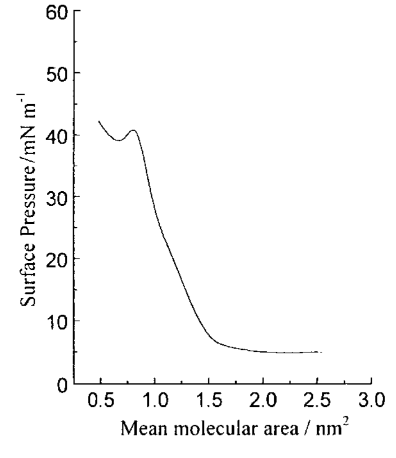


Fig. 2 The π-A isotherms of 18-crown-6 substituted phthalocyanine on a water surface.

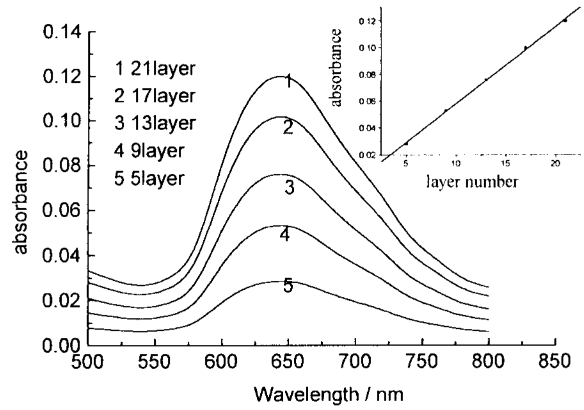


Fig. 3 Absorption spectra of the LB film with different layer numbers (the inset shows the changes of the absorbance at 650 nm *vs.* the layer number).

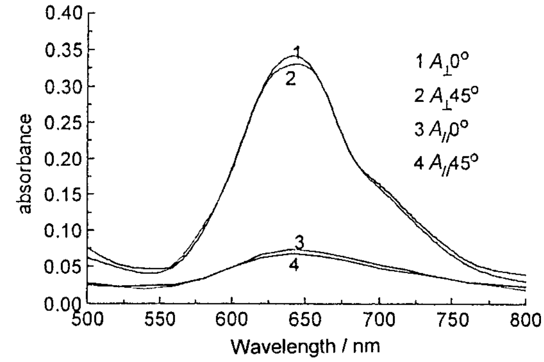


Fig. 4 Polarized absorption spectra of the LB film (21 layer on CaF_2 crystal).

Table 1 Results of the polarized absorption spectra[ab]

Incidence angle of light/°	Absorbance
0	$A_{//}$ 0.080
	$A_\perp$ 0.346
	D_o[c] 0.231
45	$A_{//}$ 0.088
	$A_\perp$ 0.345
	D_{45}[c] 0.255

[a] $n = 1.4$.[5] [b] Angle between the plane of the phthalocyanine ring and the surface of the substrate, θ, is 55°. [c] $D = A_{\|}/A_\perp$.

The gas sensing properties of the LB film

The semi-conductance of the LB film will increase significantly when exposed to NO_2 in air and will recover to the original state when exposed to fresh air. The gas sensing properties include the response time, the recovery time and the changes of the conductance.[17] The gas sensing properties of the film are listed in Table 2. The results indicate that this kind of film possesses very good gas sensing properties to NO_2 at room temperature with a quick response and reversal process. It can detect 2.5 ppm NO_2 in air.

The response and recovery process are distinctively quick compared with those of mono 15-crown-5 substituted phthalocyanine LB films.[17] It is believed that the electron transfer reactions between phthalocyanine and NO_2 are a response to increasing conductance.[4] The response process can be divided into three steps. The first one is the molecule of NO_2 diffusing to the surface of the film. The second step is the NO_2 molecules diffusing into the body of the film and the third step is the electron transfer reaction between NO_2 and phthalocyanine. The first and the third steps are very quick processes. The

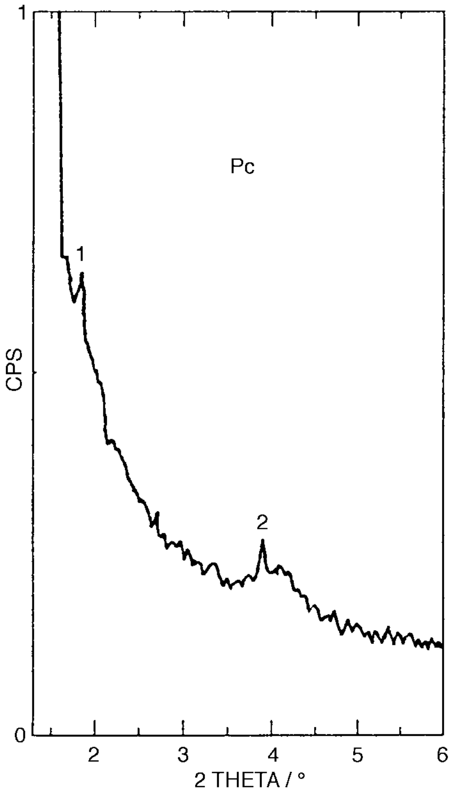


Fig. 5 X-ray diffraction patterns of the LB film (21 layer on CaF_2 crystal).

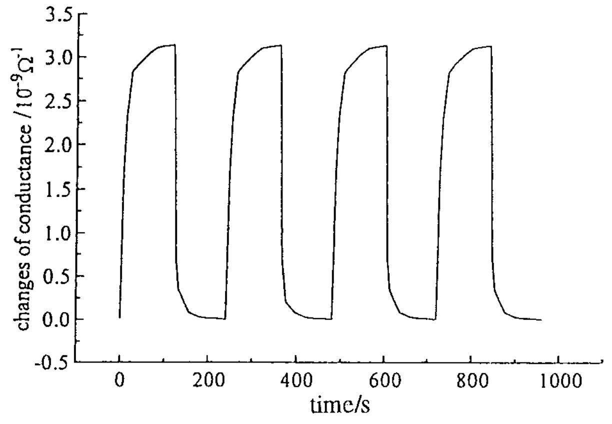


Fig. 6 The response cycles of the film to 5 ppm NO_2 in air.

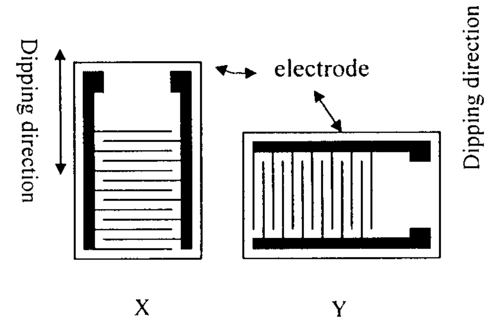


Fig. 7 The different dipping directions.

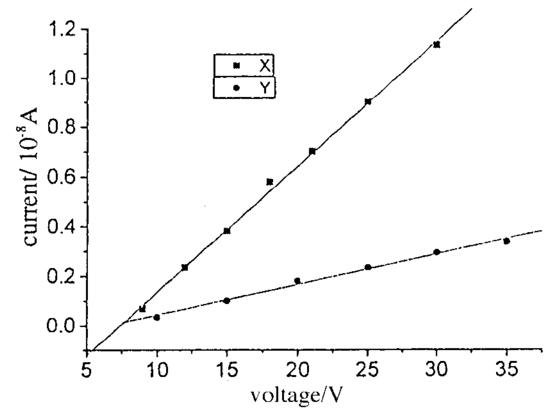


Fig. 8 The conductance anisotropy of the LB film (21 layer).

slowest step is the diffusion of NO_2 in the film which determines the rate of response. The big spaces between the molecules in the LB film of **1** provide routes for the diffusion of NO_2 and the molecules of NO_2 can easily reach phthalocyanine molecules and be adsorbed to them. So the response is quick. The fast reversal process is also ascribed to the fact that the molecules of air can be easily diffused into the film and substitute the molecules of NO_2 which are adsorbed on the molecules of phthalocyanine.

For the purpose of determining the stability of the response we exposed the LB film to 5 ppm NO_2 for 2 min and then to fresh air for 2 min, repeating the process many times. Fig. 6 shows a few cycles of these experiments. The results indicate that the response is stable and no change in the response was observed.

Anisotropy of the film's gas sensing properties

The LB films on the surface of the electrode with different dipping directions (Fig. 7) display different conductances (Fig. 8). The conductance of the film in the direction parallel to the axis of the phthalocyanine aggregates is bigger than that of the perpendicular direction. The difference in conductance induced the different responses to NO_2 (Fig. 9). The films prepared by dipping in the X direction display good conductivity and also display a big response. The anisotropy of the conductance and the gas sensing properties provide more evidence for the phthalocyanine molecules being in a highly ordered arrangement in the LB film.

Conclusion

18-Crown-6 substituted phthalocyanine **1** can form a very stable monolayer on a water surface and the monolayer can be transferred to different substrates easily by a vertical dipping method. The π-A isotherms and the absorption spectra of the

Table 2 The response behaviour of the LB film (21 layer) to NO_2 with different concentrations[a]

Concentration of NO_2 in air (ppm)	Time for response/s[b]	Time for recovery/s[c]	Changes of the conductance/$10^{-9}\Omega^{-1}$
10	3	54	3.9
5	3	42	3.6
2.5	4	45	3.4

[a] With an 8 V additional voltage on the LB film. [b] The response time is defined as the time after a 50% change in the stationary signal of the conductance. [c] The recovery time is defined as the time needed for the conductance of the film to decrease to the zero point in fresh air.

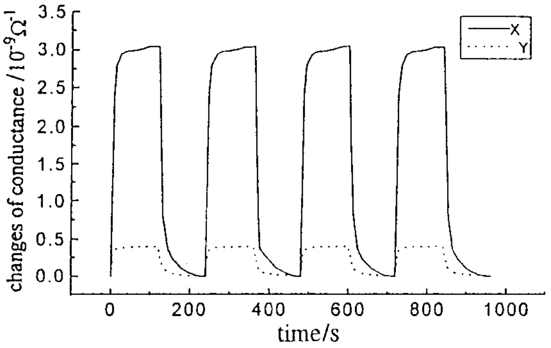
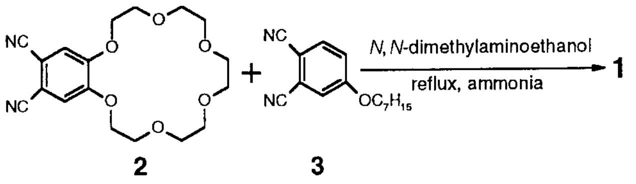


Fig. 9 The gas sensing anisotropy of the LB film (21 layer) to 10 ppm NO_2.



Scheme 1 Synthesis of the crown ether substituted phthalocyanine.

LB film show that there is a big gap between the molecules of phthalocyanine. This big gap provides ways for the diffusion of NO_2 in the film. This kind of film displays very good gas sensing properties to NO_2 in air with a quick response, a complete and quick reversal process and a relatively high sensitivity. The conductance and the gas sensing properties of the LB film display a bigger anisotropy which provide evidence for the LB film having a highly ordered structure.

Experimental

Materials

The solvents and materials used in the synthesis were all of analytical grade and were used without further purification except where specified.

The synthesis of the 18-crown-6 substituted phthalocyanine (**1**) is shown in Scheme 1. It was prepared from the mixed condensation of 4,5-dicyanobenzo-18-crown-6 (**2**) and 4-heptyloxyphthalonitrile (**3**)[15] (mole ratio 1 : 9) in *N*,*N*-dimethylaminoethanol with vigorous refluxing under the protection of ammonia gas for 12 h. The solvent was removed under reduced pressure then the product was purified by column chromatography on silica gel several times (with chloroform–methanol 9 : 1 as eluent). The second fraction was collected and evaporated to dryness to give compound **1** in 3% yield based on **2**. *m*/*z* (FAB): 1113 ($M^+ + Na^+$); ^1H NMR (300 Hz, $CDCl_3$) δ 7.3–7.9 (11H, br), 4.0–4.5 (20H, br), 2.35 (6H, m), 1.5 (30H, m), 1.15 (9H, m); elemental analysis calcd. for $C_{63}H_{78}N_8O_9$: C 69.36, H 7.16, N 10.28; found: C 69.27, H 7.23, N 10.36%.

Instruments and experimental methods

The monolayers were prepared by spreading a chloroform solution of the phthalocyanine with a concentration of 10^{-3} mol L^{-1} on water (doubly distilled, resistivity greater than 18 mΩ cm^{-1}) surface. The π-A isotherms were recorded on a KSV-5000 twin-compartment LB set. The compression speed of the barrier is 6 mm min^{-1}. The LB films were prepared by a vertical dipping method with a dipping speed of 5 mm min^{-1} and the surface pressures were kept at 30 mN m^{-1}. The LB films for the characterization of the structure were deposited on a CaF_2 or silicon crystal. The LB films for the gas sensing determination were deposited on a glass substrate bearing interdigital electrodes consisting of 50 finger pairs of electrodes (the structure and the preparation of the interdigital electrode are illustrated in ref. 8).

UV–vis absorption spectra of the film were recorded on a Hitachi 557 spectrometer and the polarized spectra were determined by adding a polariscope in the light path. Low angle X-ray diffraction experiments were carried out on a D/max-rA X-ray diffraction meter; a Cu Kα ray was used with a Ni filter. The scan range is 1.3 to 15°.

The lateral conductance and dynamic gas sensing response characteristics of the LB films were determined using a laboratory made instrument (structure and principles are illustrated in ref. 8). All the experiments were carried out at room temperature (25–30 °C)[16] and the air of the laboratory was used as the 'fresh air' without further purification and drying.

Acknowledgements

We thank Professor A. D. Lu and Professor D. P. Jiang for the help they provided in the determination of gas sensing properties and Professors Q. F. Zhou and S. Y. Shen for helpful discussions. We also thank The National Natural Science Foundation of China for financial support.

References

1 (*a*) C. C. Leznoff and A. B. P. Lever, *Phthalocyanines, Properties and Applications*, Vol. 1–3, VCH, New York, 1988–1993; (*b*) J. E. Kuder, *J. Imaging Sci.*, 1988, **32**, 51; (*c*) R. Ao. L. Kummert and D. Haarer, *Adv. Mater.*, 1995, **5**, 495; (*d*) J. D. Wright, *Prog. Surf. Sci.*, 1989, **31**, 1; (*e*) D. Wohrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129; (*f*) C. S. Frampton, J. M. O'Connor, J. Peterson and J. Silver, *Displays*, 1988, 174.
2 M. C. Petty, *Thin Solid Films*, 1992, **210–211**, 417.
3 T. Moriizumi, *Thin Solid Films*, 1988, **160**, 413.
4 R. Rella, A. Serra, P. Siciliano, A. Tepore, L. Valli and A. Zocco, *Thin Solid Films*, 1996, **286**, 256.
5 D. P. Jiang, A. D. Lu, Y. J. Li and Y. Fan, *Thin Solid Films*, 1991, **199**, 323.
6 D. Campbell and R. A. Colins, *Thin Solid Films*, 1997, **295**, 227.
7 P. Roisin, J. D. Wright, R. J. M. Nolte, O. E. Sieicken and S. C. Thorpe, *J. Mater. Chem.*, 1992, **2**(1), 131.
8 A. D. Lu, L. G. Zhang, D. P. Jiang, Y. J. Li and Y. Fan, *Thin Solid Films*, 1994, **244**, 955.
9 A. R. Coray, V. Ahsen and O. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932.
10 R. Hendriks, O. E. Sielcken, E. Drenth and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1986, 1264.
11 G. Gumus, Z. Z. Ozturk, V. Ahsen, A. Gul and O. Bekaroglu, *J. Chem. Soc., Dalton. Trans.*, 1992, 2485.
12 H. J. Xu and G. X. Xiong, *J. Photochem. Photobiol., A. Chem.*, 1995, **92**, 35.
13 N. Kabayashi, M. Togashi, T. Osa, K. Ishii, S. Yamauchi and H. Hino, *J. Am. Chem. Soc.*, 1996, **118**, 1073.
14 J. D. Wright, P. Roisin, G. B. Rigby, E. Erkizia, R. J. M. Nolte and S. C. Thorpe, *Sens. Actuators B*, 1993, **15–16**, 301.
15 X. Y. Li, G. X. Xiong and H. J. Xu, *Chin. Chem. Lett.*, 1998, **8**(9), 815.
16 M. Fujiki, H. Tabei and T. Kurihara, *Langmuir*, 1988, **4**, 1123.
17 X. Y. Li, S. Y. Shen, Q. F. Zhou, H. J. Xu, A. D. Lu and D. P. Jiang, *Thin Solid Films*, 1998, **324**, 274.
18 M. Yoneyama, M. Sugi and M. Saito, *Jpn. J. Appl. Phys.*, 1985, **25**, 961.

Paper 9/01887E