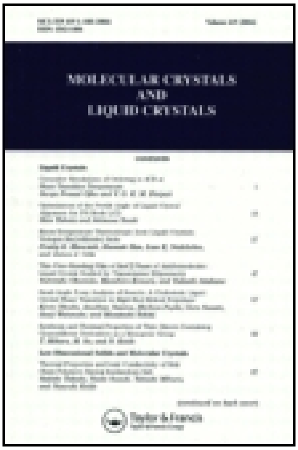

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# A Novel Amphiphilic Zinc Phthalocyanine LB Flms as Gas Sensor Material and its Interaction with $NH_3$

Ximing Ding [a] , Huijun Xu [a] , Ligong Zhang [b] , Dapeng Jiang [b] & Ande Lu [b]

[a] Institute of Photographic Chemistry, Beijing, 100101, China

[b] Changchun Institute of Physics, Changchun, 130021, China

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# A Novel Amphiphilic Zinc Phthalocyanine LB Flms as Gas Sensor Material and its Interaction with $NH_3$

XIMING DING[a], HUIJUN XU[a*], LIGONG ZHANG[b], DAPENG JIANG[b] and ANDE LU[b]

[a]*Institute of Photographic Chemistry, Beijing 100101, China and* [b]*Changchun Institute of Physics, Changchun 130021, China*

Two kinds of amphiphilic phthalocyanines(AmPc,AmPcZn) have been deposited as smooth and well ordered LB films. Absorption spectra show that AmPc films are consistent with a stacked cofacial columnar structure while the AmPcZn films consist of aggregates with weakly interacting molecules. These two films exhibit different behavior toward $NH_3$ gas-sensing. AmPcZn films gave strong and fast response on exposure to $NH_3$ whereas AmPc films showed very weak response. It is proposed that coordination of $NH_3$ by AmPcZn results in lowering the energy gap and hence the activation energy of AmpcZn that account for the larger increase in conductance of AmpcZn films compared with AmPc films.

*Keywords:* phthalocyanine; LB films; gas-sensor

## INTRODUCTION

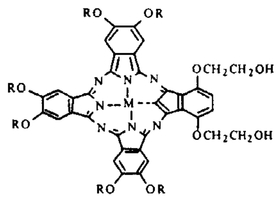
It has long been known that the conductivity of phthalocyanines is very sensitive to the presence of certain gases which leads to increasing interest in their use as gas-sensor materials[1]. There are many factors such as structure and morphology of the phthalocyanine films that exert influence on the conductivity change. It is believed that the peripheral substituents[2] as well as central metal atom[3] of phthalocyanines play important roles in the gas-sensing behavior of phthalocyanine LB films. Previously, we reported the synthesis of a series of metal free amphiphilic phthalocyanines(AmPc)[4] and the gas-sensing behavior of phthalocyanine LB films[5]. They showed very fast

* to whom correspondence should be addressed

and strong response to $NO_2$ at room temperature and weak response to $NH_3$. In searching for an element to detect $NH_3$, 1,4-di(2-hydroxyethoxy) 9,10,16,17,23,24-hexapentoxyphthalocyanine zinc(AmPcZn) has been synthesized. In this paper the interaction of AmPcZn films with $NH_3$ compared with its metal free precursors was studied. The effect of ammonia coordination with AmPcZn on the conductance variations is discussed.

## EXPERIMENTAL

Fig.1 gives the structure of AmPcZn. The synthesis of the compounds will be reported elsewhere.



R=$CH_2(CH_2)_3CH_3$
M=2H, AmPc, M=Zn, AmPcZn

FIGURE1 Structure of the titled compounds

### Instrument and Methods

UV-visible absorption spectra were measured on a Hitachi 557 UV-visible spectrometer. A KSV-5000 twin-compartment LB trough was used for the preparation of LB films. The LB films were built up on glass and/or aluminum interdigital electrodes for spectroscopy and conductance measurements. A constant surface pressure of 30mN/m was maintained, resulting in fairly good deposition of typical Y-type films with transfer ratio being about 0.8-1.0.

The lateral conductance of the LB films and dynamic gas-sensing response characteristic were monitored using a current-voltage(*I-V*) measuring apparatus, the details of which have been reported elsewhere [5].

## RESULTS AND DISCUSSION

### UV-vis spectra of the LB Films

The monolayers of the titled compounds were transferred to the substrate by vertical lifting method at 30mN/m with transfer ratio of 0.8-1.0 giving Y-type films. Fig.2 gives the UV-visible absorption spectra of the multilayers compared with solution spectrum. Inset is the plot of maximum absorbance *vs.* the number of layers. For AmPc, the monomer Q band absorption peaks appear at 670nm and 705nm in solution and it is broadened and strong hypsochromically shifted in the direction of around 620nm is observed as the consequence of molecular association with cofacial macroring orientation in the LB films[6]. In contrast, the spectra of AmPcZn show very little shift consistent with aggregates with weakly interacting molecules indicating that the AmPcZn LB films are less packed.

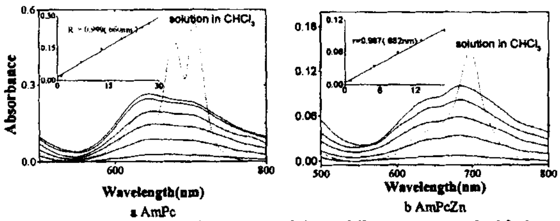



**FIGURE.2 The absorption spectra of the multilayers compared with the solution spectrum(inset is the plot of the absorbance vs. the number of layers)**

## $NH_3$ Gas-sensing Behavior

The conductance of compound AmPc LB films showed little change when exposed to 10ppm $NH_3$. In the case of AmPcZn, the LB films exhibit very strong and fast response to $NH_3$ at room temperature. Fig.3 gives the response behavior of 9-layer AmPcZn LB films to different concentration of $NH_3$ gas. R.Rella presented a model for active layer-gas interaction[2]. A relationship in which the conductivity of Pc LB films is proportional to the power of the adsorbed gas partial pressure is obtained:

$$\frac{\sigma_{gas}}{\sigma_{air}} \infty P_{NO_2}^{\beta} \qquad [1]$$

The equation also fits well our experimental results for AmPcZn films as shown in fig.3. Plotting $\ln(\sigma_{gas}/\sigma_{air})$ *vs.* $\ln P_{NH3}$, a straight line is obtained with linear coefficient of 0.997. A similar relation has also been found using AmPc. As one can see, the AmPcZn films exhibit higher sensitivity to $NH_3$ with a slope($\beta$ value) of about 0.55 and lower sensitivity threshold of about 1ppm, the value obtained for the intercept at $\sigma_{gas}/\sigma_{air}=1$. On the other hand, the AmPc LB films show lower sensitivity with a slope $\beta=0.25$ and higher sensitivity threshold of about 5ppm. We believed that the difference in $NH_3$ gas-sensing behavior of the two LB films is attributed to the coordination of $NH_3$ molecule with AmPcZn. It is generally accepted that $O_2$ is an almost unavoidable dopant of phthalocyanine thin films resulting in a weak charge transfer equilibrium:

$$Pc + O_2 \rightleftharpoons (Pc^{\delta+} \text{---} O_2^{\delta-}) \rightleftharpoons \text{free carrier}$$

which is largely displaced to the left side. The increase of film conductance is comparably small in the case of AmPc. We suggest that on legation by $NH_3$, the energy gap of AmpcZn and hence the activation energy is lowered, so that the equilibrium will be shifted to the right. The charge carrier thus created lead to the increase of conductance of the AmPcZn LB films.

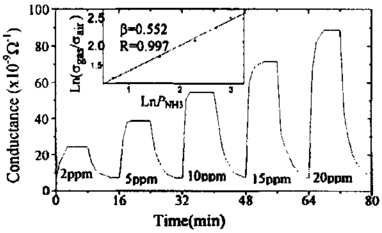


FIGURE.3 The response behavior of 9-layer LB films of compound **b** to $NH_3$ of different concentration

## CONCLUSION

A novel amphiphlic phthalocyanine and its zinc complex LB films have been studied as $NH_3$ gas sensor material. The former films gave very weak response to $NH_3$ whereas the latter showed strong and fast response. The difference in gas-sensing behavior is attributed to the coordination of $NH_3$ molecule by AmPcZn resulting in lowering the activation energy for the charge transfer process. The charge carrier movement is thus facilitated and the conductance of the films increased.

**Acknowledgments**

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