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The effects of detected gases on spectroscopic properties of phthalocyanine Langmuir–Blodgett films

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Abstract

Tetrakis-4-(2,4-di-amylphenoxy) phthalocyaninato-polysiloxane (R_4PcPS) was derived from the correspondingly substituted phthalocyaninatosilicon hydroxide ($R_4PcSi(OH)_2$). The photoluminescence and excitation spectra of R_4PcPS and $P_4PcSi(OH)_2$ solutions in chloroform were shown. The absorption spectra of R_4PcPS Langmuir–Blodgett films, before and after adsorbing I_2, were compared. The infrared absorption spectra of an asymmetrically substituted copper [tri-4-(2,4-di-amylenoxy)-mono-4-(2-methoxyethoxy)] phthalocyanine (AsyCuPc) Langmuir–Blodgett films, before and after adsorbing NH_3, were studied.

Keywords: Adsorption; Langmuir–Blodgett films; Optical properties; Sensors

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1. Introduction

Change of electrical conductivity induced by adsorbing various gases, such as NO_2, NH_3, Cl_2 and I_2, on Langmuir–Blodgett (LB) and vacuum-sublimated films of metal phthalocyanines (MPc) provided a mean of detecting these gases in air [1–9]. Gas-sensitive properties of MPc were widely studied and the gas sensors based on metal phthalocyanines have shown high enough sensitivity to some gases. But their spectroscopic properties related to adsorption of detected gas were rarely investigated. In the previous papers, we have reported some preliminary results on morphology, structure, gas-sensitive and dynamic properties of monomeric substituted copper phthalocyanine [7,10–12]. Recently, tetrakis-4-(2,4-di-amylphenoxy) phthalocyaninato-polysiloxane (R_4PcPS) was derived from the correspondingly substituted phthalocyaninato silicon hydroxide ($R_4PcSi(OH)_2$) [13]. In this study, the photoluminescence and excitation spectra of $R_4PcSi(OH)_2$ and R_4PcPS solutions in chloroform were shown. The spectroscopic properties of R_4PcPS LB films, before and after adsorbing I_2, were compared. On the other hand, the infrared spectroscopic properties of an asymmetrically substituted copper (tri-4-(2,4-di-amylenoxy)-mono-4-(2-methoxyethoxy)) phthalocyanine (AsyCuPc) LB film, before and after adsorbing NH_3, were studied.

2. Experimental details

2.1. The preparation of LB films and sample chamber

The synthesis of R_4PcPS and AsyCuPc were reported in previous papers [13,14]. The LB films of R_4PcPS and AsyCuPc were deposited with a KSV-5000 Langmuir trough. The spreading solutions were prepared by dissolving the R_4PcPS and AsyCuPc in chloroform. The concentrations of the R_4PcPS and AsyCuPc solutions were all 1 mg cm^{-3}. The R_4PcPS LB film deposition parameters used in this study were as follows: surface pressure, 17 mN m^{-1}; pH, 8.2; dipping speed, 5 mm min^{-1}; subphase temperature, 20 °C. A 15-layer R_4PcPS LB film was prepared onto a quartz substrate for the measurements of absorption spectra. Z-type deposition was observed from the recording curves monitoring deposition processes. The LB deposition parameters for AsyCuPc were as follows: surface pressure, 20 mN m^{-1}; pH, 8.0; dipping speed, 5 mm min^{-1}; subphase temperature, 19 °C. A 22-layer AsyCuPc LB film was deposited onto CaF_2 substrate for the measurement of infrared absorption spectra.

The structure of the sample chamber used for spectroscopic measurement is shown in Fig. 1. The two substrates including LB films and a glass frame were glued together and the LB films faced the inside of the sample chamber as shown in Fig. 1. The detected gas was injected into the sample chamber through a hole, then the hole was sealed.

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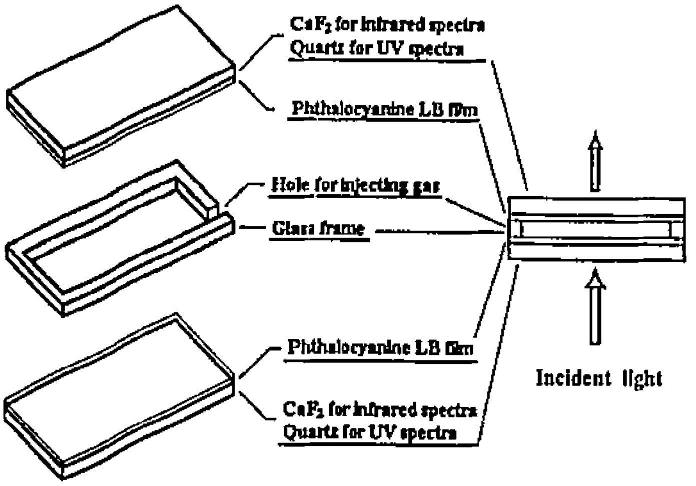

Fig. 1. The structure of the sample chamber.

2.2. The spectral measurement

The photoluminescence (PL) and excitation (Ex) spectra of $R_4PcSi(OH)_2$ and R_4PcPS solutions in chloroform were measured with a F-4000 Fluorescence Spectrophotometer. The absorption and PL spectra of R_4PcPS LB films, before and after adsorbing I_2, were measured with a UV-360 Recording Spectrophotometer and a F-4000 Fluorescence Spectrophotometer respectively. The infrared (IR) absorption spectra of AsyCuPc LB films, before and after adsorbing NH_3, were measured with a BIO-RAD FTS-7 Spectrometer.

3. Results and discussion

3.1. The spectroscopic properties of $R_4PcSi(OH)_2$ and R_4PcPS solutions in chloroform

It was observed that the PL and Ex spectra of $R_4PcSi(OH)_2$ and R_4PcPS solutions in chloroform are different. Under the excitation of 350 nm (xenon lamp), two PL peaks of $R_4PcSi(OH)_2$ solution in chloroform appear at 709 nm and 775 nm respectively, as shown in Fig. 2. The photoluminescence peak of R_4PcPS solution in chloroform is at 697 nm, under the same excitation conditions (Fig. 2). In comparison with PL of $R_4PcSi(OH)_2$, no PL peak at 775 nm appeared and a blue-shift of the PL peak from 709 nm to 697 nm occurred for polymeric R_4PcPS. The blue-shift of PL was attributed to the enhancement of the interaction between π electrons after polymerization and the increase of the energy states difference between π and π^*. The PL peak at 775 nm may have originated from hydroxyl.

The excitation spectra of $R_4PcSi(OH)_2$ and R_4PcPS solutions in chloroform are shown in Fig. 3(a) and 3(b). There

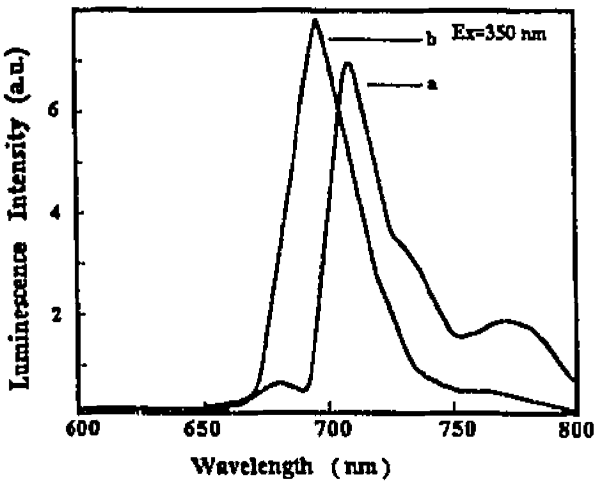

Fig. 2. Photoluminescence spectra of (a) ($R_4PcSi(OH)_2$ and (b) R_4PcPS solution in chloroform.

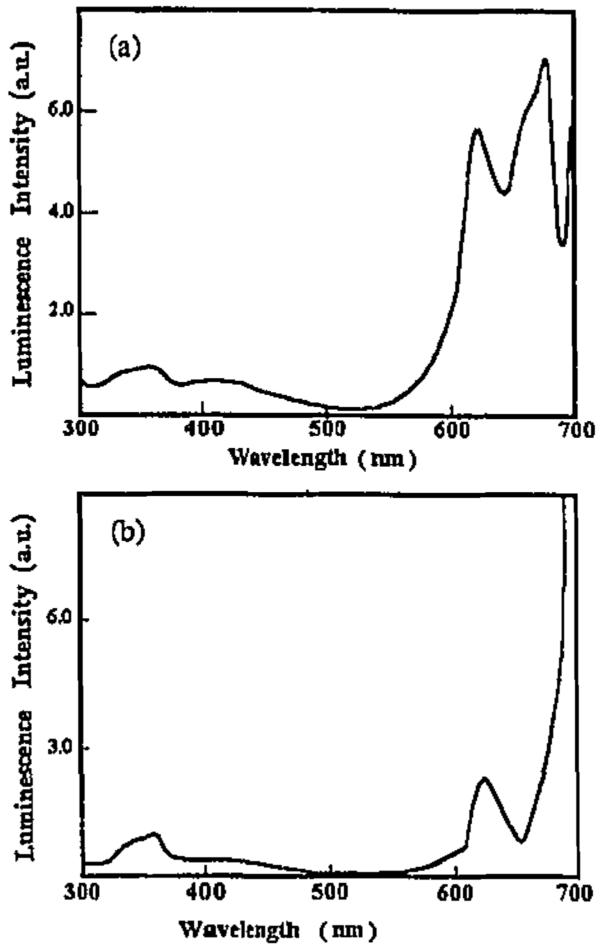

Fig. 3. (a) The excitation spectrum of $R_4PcSi(OH)_2$ solution in chloroform (luminescence measured at 709 nm). (b) The excitation spectrum of R_4PcPS solution in chloroform (luminescence measured at 698 nm).

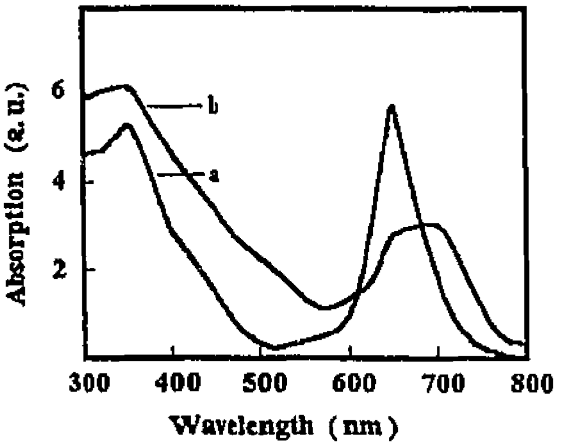

Fig. 4. The UV absorption spectra of R_4PcPS LB film (a) before and (b) after adsorbing I_2.

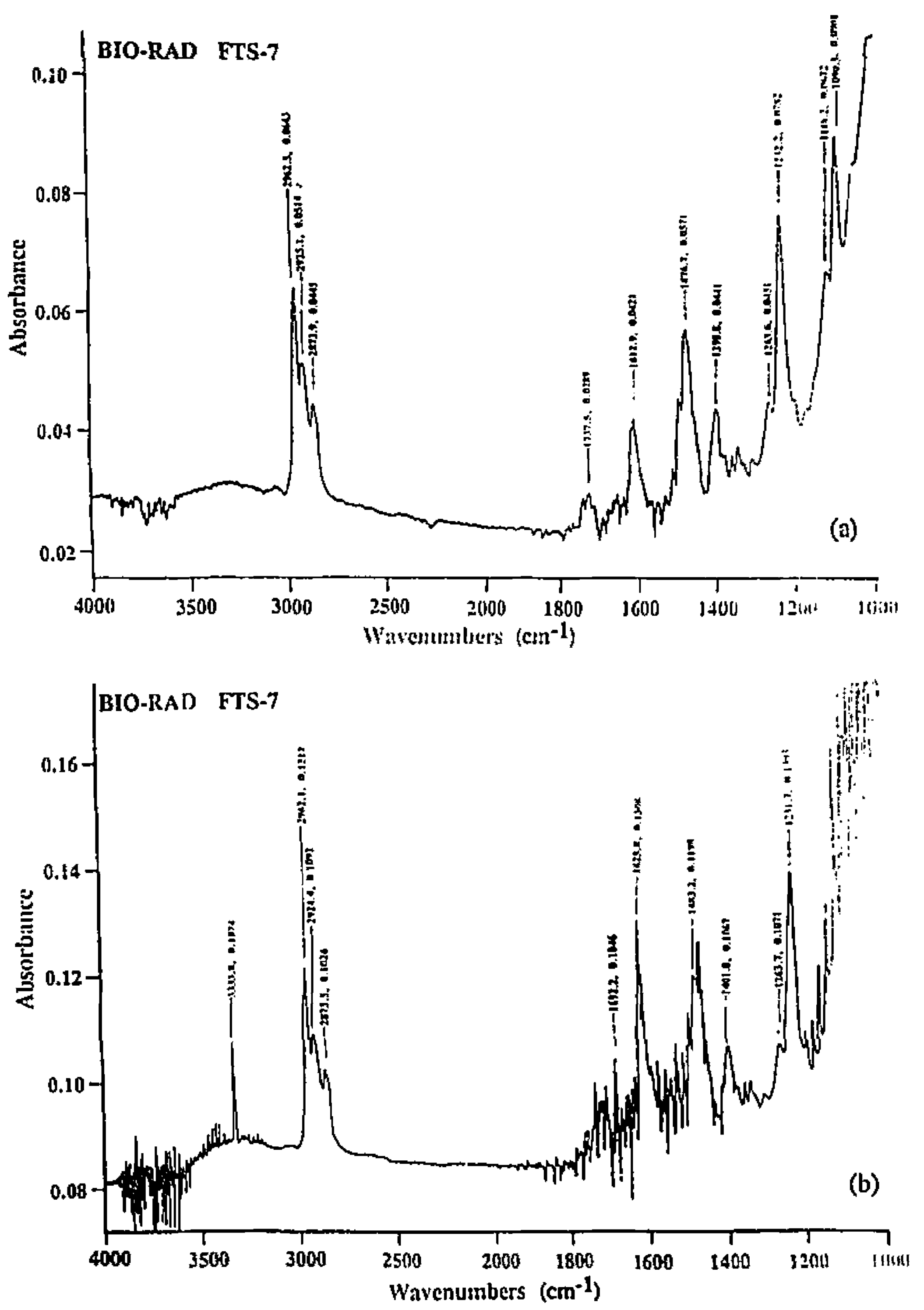

Fig. 5. (a) The infrared absorption spectrum of AsyCuPc LB film before adsorbing NH_3. (b) The infrared absorption spectrum of AsyCuPc LB film after adsorbing NH_3.

are two Ex peaks in Fig. 3(a) at 622 nm and 676 nm respectively. It was shown that the comparatively intensive photoluminescence at 709 nm of $R_4PcSi(OH)_2$ could be seen when $R_4PcSi(OH)_2$ was excited by light at 622 nm and 676 nm. After polymerization, the Ex peak at 676 nm disappeared and only the peak at 622 nm remained in Fig. 3(b). It could be said that the peak at 676 nm of $R_4PcSi(OH)_2$ originated from a hydroxyl group and the peaks at 622 nm of $R_4PcSi(OH)_2$ and R_4PcPS were caused from the phthalocyanine ring.

3.2. The spectroscopic properties of R_4PcPS LB films before and after adsorbing I_2

It was observed from Fig. 4 that a slight red-shift of the absorption peak and the broadening of the absorption band for R_4PcPS LB film occurred after adsorbing I_2. The absorption of R_4PcPS LB film was attributed to the π–π^* transition. When I_2 was adsorbed onto the surface of the R_4PcPS LB film, the interaction between the adsorbed I_2 and π electrons lead to the weakening of the interaction between π electrons.

As a result, the red-shift of the absorption peak occurred. Broadening of the absorption band is observed in Fig. 4. In the opinion of quantum mechanics, because the symmetry of R_4PcPS LB film was damaged, and the states π and π^* were split after I_2 was adsorbed, the broadening of the absorption band occurred

3.3. *The infrared absorption spectra of AsyCuPc LB films before and after adsorbing NH_3*

The infrared spectra of the AsyCuPc LB film, before and after adsorbing NH_3, are shown in Fig. 5(a) and 5(b). There are eight peaks (1232.2, 1263.7, 1398.8, 1476.6, 1612.9, 2873.9, 2925.1, 2962.5 cm^{-1}) in Fig. 5(a), i.e. before adsorbing NH_3, which are relative to phthalocyanine. After adsorbing NH_3, a new peak (3333.8 cm^{-1}) appeared, which is probably related to NH_3. On the other hand, it was observed from Fig. 5(b) that the slight shifts of the peaks (1398.8 → 1401.8, 1476.6 → 1480.2, 1612.9 → 1625.8, cm^{-1}) and the comparative enhancement of the peak at 1625.8 cm^{-1} (about three times) compared with Fig. 5(a). The absorption peaks at 1398.8, 1476.6 and 1612.9 cm^{-1} were due to vibration of $-OH$, $-CH_3$ and $-N-H$ bonds respectively. It can be considered that NH_3 was probably adsorbed onto one of the $-OH$, $-CH_3$ and $-N-H$ bonds and produced a considerable effect on $-OH$, $-CH_3$ and $-N-H$. The shifts of the peaks probably occurred because of the interaction between NH_3 and the vibrations of these bonds.

4. Conclusions

In this study, the photoluminescence and excitation spectra of $R_4PcSi(OH)_2$ and R_4PcPS solutions in chloroform were measured. The absorption of the R_4PcPS LB film, before and after adsorbing I_2, were studied. After I_2 was adsorbed onto the R_4PcPS LB film, a slight red-shift and broadening of the absorption band were obtained. The infrared absorption of the AsyCuPc LB film, before and after adsorbing NH_3, were compared. The slight shift of the vibration peaks (1398.8, 1476.6, 1612.9 cm^{-1}) and the enhancement of the peak at 1625.8 cm^{-1} (about three times) were observed as a result of interaction between NH_3 and vibration of these bonds.

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