

# Effects of organic additives on the microstructural, rheological and electrical properties of silver paste for LTCC applications

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## Research Article

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# Abstract

Zinc(II) phthalocyanine (**Zn(II)Pc**) molecule was the first time prepared onto three different substrates utilizing Langmuir-Blodgett (LB) deposition technique to investigate its vapor sensing abilities and some optical properties. We utilized five different and well-known techniques to control monolayer quality of **Zn(II)Pc** LB film. The obtained thickness and refractive index values for **Zn(II)Pc** LB film with coated at different layers vary from 3.2 to 10.9 nm and from 1.42 to 1.71, respectively. The sensing properties were investigated by exposing the **Zn(II)Pc**-based mass or optical sensor to some organic vapors. Kinetic results presented that this **Zn(II)Pc** material is a good candidate as a sensor element with a fast and reversible response for dichloromethane sensing devices.

## 1. Introduction

Phthalocyanines have been greatly preferred in many technological and scientific areas such as solar cells [1], LB films [2] and chemical sensors [3]. Presence of planar delocalized large  $18\pi$  electrons in the macrocycle and strong optical absorption in metallo phthalocyanines provide them a convenient sensing material for volatile organic compounds (VOCs) [4]. LB thin film technique plays a critical role to fabricate a sensitive thin film layer of phthalocyanine derivative for room temperature VOCs sensor applications due to its practical and controlled production [5]. Surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) methods are widely utilized as an optical sensitive and mass sensitive, respectively, for the VOCs detection using phthalocyanine LB films [6,7]. Thanks to the high sensitivity and stability of the sensitive absorption layers, phthalocyanine-based thin films have become a significant area of study in sensor applications [8].

In this paper, a new synthesized amphiphilic phthalocyanine (**Zn(II)Pc**) is selected to fabricate a sensitive and selective LB thin film layer which is used for a detection of VOCs. Dichloromethane, carbon tetrachloride, toluene and m-xylene vapors are used for sensor applications. SPR and QCM results indicated that the selectivity of **Zn(II)Pc** LB layer to dichloromethane is approximately 3.39 times for SPR and 2.69 times for QCM results higher than other vapors. The results obtained from kinetic results stated that **Zn(II)Pc**-based mass or optical sensor yields a stable and reversible response to all vapors and a selective and sensitive response to dichloromethane vapor than others.

## 2. Experiment Details

**Zn(II)Pc** molecule (Fig. 1), which is a candidate for the use of a sensor active layer, was synthesized by the following literature [9]. All **Zn(II)Pc** thin films were prepared with model 622 Nima-LB trough (area  $1200\text{ cm}^2$ ) onto three different substrates such as gold-coated glass, quartz glass and quartz crystal for SPR, UV-Vis, SEM, AFM and QCM measurements.

The properties of Langmuir for **Zn(II)Pc** molecules were examined using a NIMA 622 model LB trough. The surface pressure ( $\pi$ ) measurements as a function of the area (A) covered by the **Zn(II)Pc** molecules

dissolved in chloroform. This solution at a concentration of  $1 \text{ mg mL}^{-1}$  was slowly dripped into the trough, whose water surface was controlled for cleanliness ( $0 < \pi < 0.1$ ), using microliter syringe (Hamilton). The LB trough (made of Teflon materials) consists of Wilhelmy, which is used as a pressure sensor, and two barriers, one of which is movable. This barrier compression speed has been determined in the literature to be a suitable value to avoid instability effects [10-12]. After waiting approximately 15 minutes for the chloroform in solution to evaporate, the moving barrier was allowed to compress the monolayer at the air / water interface towards the center of the trough. Isotherms obtained as a result of compression of the Langmuir monolayer at the air / water interface are characterized by certain regions such as gas phase, liquid phase, solid phase and collapse. The process of all **Zn(II)Pc** LB layer deposition was fixed by determining a convenient surface pressure value of  $25 \text{ mN m}^{-1}$  from isotherm graph (Fig. S1).

The process of **Zn(II)Pc** LB layer deposition onto solid substrates was started after the determination of a suitable surface pressure. LB thin film transfer curve is a critical parameter for monitoring the deposition process, and the first four layer transfer graph of **Zn(II)Pc** monolayer within the scope of the paper is given in Fig. 2. The analysis of this process is carried out by calculating the transfer rate (TR) shown in Equation 1.

$$\text{TR} = \frac{A_1}{A_2} \quad (1)$$

$A_1$  is the decrease in the area covered by a monolayer on the water surface and  $A_2$  is the area of the thin film coated on the substrate. The TR value was calculated as  $\sim 0.93$  for **Zn(II)Pc** LB thin film. This value is proof that homogeneous LB thin films have been successfully produced.

The chemical sensing abilities of **Zn(II)Pc** LB thin film sensor were actualized *via* SPR and QCM technique. The detailed information about these techniques was reported in the part of Supplementary Data (Fig. S2).

## 3. Results And Discussion

### 3.1 UV-Visible Results

The absorption spectra of **Zn(II)Pc** chloroform solution using different concentration and **Zn(II)Pc** LB thin film multilayers prepared onto quartz glass substrate was obtained by UV-vis spectrometer and results represented in Fig. S3 and Fig. 3, respectively. Two absorption bands attributed to  $\pi-\pi^*$  transition (the Soret (B) and the Q-band) of the **Zn(II)Pc** molecules were observed at 269 nm and 684 nm both **Zn(II)Pc** solution and LB thin film multilayers. The inset in Fig. 3 shows the correlation between number of layers and the change of absorption values. This linear proportionality between them has supported that deposition takes place during coating for each layer and coating is very sustainable for each bilayer.

### 3.2 QCM results

In this work, the Y-type **Zn(II)Pc** LB films were fabricated in a symmetrical mode onto quartz crystal substrate (Fig. 4). The inset in Fig. 4 presents linearity between the frequency change and **Zn(II)Pc** LB layers with a linear regression of 0.9923. This linearity demonstrated that each **Zn(II)Pc** bilayer could be successfully deposited and almost equal mass was coated onto the substrate. The frequency change for each layer (27.17 Hz/layer) and the mass coated onto the substrate for each layer (435.124 ng/layer) could be determined from the data of the inset in Fig. 4 and by utilizing Sauerbrey equation [13].

### 3.3 SPR results

SPR system was utilized to evidence the deposition of **Zn(II)Pc** LB monolayer onto gold-coated substrate. The SPR curves of **Zn(II)Pc** LB thin films are represented in Fig. S4 and these curves (from 2 layers to 10 layers) shift to from the left to the right. The inset in Fig. S4 presents the linear relationship between the shifts in the angle of incidence and **Zn(II)Pc** LB layers. A linear regression of 0.9884 indicates that **Zn(II)Pc** LB films were fabricated onto the substrate successfully and homogeneously. The experimentally measured SPR curves of **Zn(II)Pc** LB films were fitted *via* Winspall software to determine the values of refractive index and thickness for **Zn(II)Pc**-coated thin films. The fitted SPR curves for **Zn(II)Pc**-coated four LB film layers and bare gold were given in Fig. 5. Similar fitting process was fixed for other **Zn(II)Pc** LB layers. The inset in Fig. 5 provided similar results compared with UV-Vis and QCM results by obtaining of the linear relationship. As seen in Table 1 and the inset of Fig. 5, the values of **Zn(II)Pc** LB film thickness or refractive index demonstrate a rise depending on the **Zn(II)Pc** LB layers.

**Table 1** The thickness and refractive index of **Zn(II)Pc** thin films.

	Number of LB layers	Thickness (nm)	Refractive index
<b>Zn(II)Pc LB thin film</b>	2 layer	3.2	1.41
	4 layer	5.6	1.53
	6 layer	7.4	1.61
	8 layer	9.5	1.66
	10 layer	10.9	1.72

### 3.4 AFM and SEM results

AFM measurements were taken to analyze the surface morphology of **Zn(II)Pc** LB thin film with 2D and 3D AFM images in the surface area of 10x10  $\mu\text{m}^2$  (Fig. 6). The RMS roughness, mean roughness and maximum height values of the surface were observed as 3.8, 2.85 and 14.96 nm for the image recorded with the dimensions 10  $\mu\text{m}$  x 10  $\mu\text{m}$ , respectively. The **Zn(II)Pc** LB film surfaces, containing some roughness structure, provide VOCs molecules to penetrate into deeper layer in vapor sensing application. SEM images of non-coated bare glass and **Zn(II)Pc** LB film coated glass were obtained for the supporting of the LB films fabricated. While Fig. S5a displays the SEM image for bare glass (non-coated), the SEM image given in Fig. S5b proves the matrix of **Zn(II)Pc** can be formed in the thin film.

### 3.5 Kinetic Measurements of the Optical/Mass Chemical Sensor

SPR technique is used to monitor a host-guest interaction between the **Zn(II)Pc**-based chemical sensor and VOCs by recording the photodetector responses (Fig. 7). Some harmful VOCs, namely, toluene, m-xylene, carbon tetrachloride and dichloromethane were released into the space of gas cell for 120 seconds, in order of air-vapor-air-vapor...-air, periodically. The responses of LB film to all vapors suddenly increased by several seconds (*adsorption process*) and then an exponential decrease was observed due to the *diffusion process*. This rapid change can be resulted from two important reasons. The first, the shift of background refractive index, which depends on the concentration of vapor, may be asserted. The surface effect between **Zn(II)Pc** LB film surface and vapor molecules can be stated as the second reason. Similar kinetic study was carried out using QCM technique for supporting SPR kinetic results. From the Fig. 7 and Fig. S6, the comparatively large response values obtained from SPR and QCM measurements for dichloromethane are noteworthy among used vapors at saturated concentration. The SPR/QCM kinetic results of the **Zn(II)Pc**-based chemical sensor to dichloromethane vapor was presented in Fig. S7 and Fig. S8 to observe the repeatability and renewability properties of **Zn(II)Pc** LB film chemical sensor by running three times of this process. These kinetic results show that **Zn(II)Pc** chemical sensor are reproducible for dichloromethane vapor. Similar the host-guest interaction was recorded at different concentration of dichloromethane represented in Fig. S9.

The results of all kinetic measurements can be expressed through the vapor pressure and the molar volume of VOCs given in Table 2, and dichloromethane vapor has the biggest vapor pressure (at 20 °C) and molar volume among used in this work. Since dichloromethane molecules have the highest vapor pressure and the lowest molar volume among VOCs used in this work, their diffusions into the **Zn(II)Pc** LB film is the easiest. The values of the kinetic responses for the other vapors (carbon tetrachloride, toluene and m-xylene) are lower than dichloromethane vapor due to the effect of these physical properties. Therefore, the other vapors with the highest molar volume cannot easily penetrate into the **Zn(II)Pc** LB thin film sensor material when compared with the diffusion of dichloromethane vapor into the same thin film.

**Table 2** Physical properties of organic vapors and kinetic responses.

Organic vapors	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )	Vapor pressure (kPa, 20 °C)	Photodetector response change, ( $\Delta I$ )	Frequency shift, ( $\Delta f$ )
Dichloromethane	64.10	46.50	0.148	78
Carbon tetrachloride	97.10	12.00	0.044	29
Toluene	107.10	2.91	0.037	27
m-xylene	122.00	0.80	0.016	24

## 4. Conclusions

The structural characterization and the preparation quality of **Zn(II)Pc** LB thin film layers were examined by (i) the mass change onto quartz crystal (ii) the shift of the UV-Vis absorption spectra (iii) the change of resonance angle in the SPR curves, and (iv) SEM/AFM imaging techniques. The results obtained from all characterization techniques aforementioned in related parts prove that the fabrication of **Zn(II)Pc**-based thin films onto the different substrates was successfully and uniformly achieved with linear regressions vary from 0.9884 to 0.9957. Some optical properties of **Zn(II)Pc** materials were also illuminated with this study. The sensing behaviors of **Zn(II)Pc** chemical sensor against to some VOCs were investigated by utilizing QCM and SPR techniques. These kinetic results present that **Zn(II)Pc**-coated chemical sensor exhibits higher sensitive and selective response to dichloromethane vapor than other vapors.

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