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Calix[4]amine Langmuir-Blodgett thin film sensing properties against volatile organic compounds

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Abstract. Thin films of CBAMINE were deposited at air-water interface by the method of Langmuir-Blodgett (LB) technique onto a suitable substrate. Atomic force microscopy technique was used to characterize its thin film properties. The results indicate that a uniform LB film monolayer from the water surface to a glass or quartz crystal substrates deposited with a transfer ratio of over 96 %. Gas sensing properties and thickness of the LB thin films of CBAMINE were investigated using Surface plasmon resonance (SPR) technique. Its vapour sensing properties were investigated for different volatile organic compounds. Reversible changes in the optical behaviour were observed and thin films of this material are highly selective for chloroform vapour with fast response and recovery times.

1. Introduction

Carbon-containing volatile organic compounds (VOCs) are quickly evaporated into the atmosphere once emitted. While coming from certain solids or liquids, VOCs are released as gases into the atmosphere. VOCs are a source of both indoor and outdoor pollution. As an indoor pollution, VOCs may be named to as volatile organic chemicals. Indoors, VOCs evaporate under normal indoor atmospheric conditions according to temperature and pressure. VOCs may also be very dangerous as the outdoor pollutants

As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed [1]. Due to this reason, gas sensor technology has advanced quite rapidly during past few decades [2-4].

In this study, the SPR method [5] was preferred for VOCs sensing examination of the medium. It is one of the most sensitive detection methods for changes of thicknesses and refractive index in ultra-thin films and is a convenient optical transduction technique widely utilised in molecular recognition. In our study, the CBAMINE material, a calixarene derivative, was used as the receptor [6]. The chemical structure of this molecule is shown in figure 1. Molecular behaviour as a thin film of CBAMINE was investigated using Langmuir-Blodgett (LB) thin film method. Gas sensing behaviour of LB thin films of CBAMINE was investigated using SPR. This article also reports the results obtained from UV-visible spectroscopy and atomic force microscopy (AFM) measurements for the characterization of CMAMINE LB films.

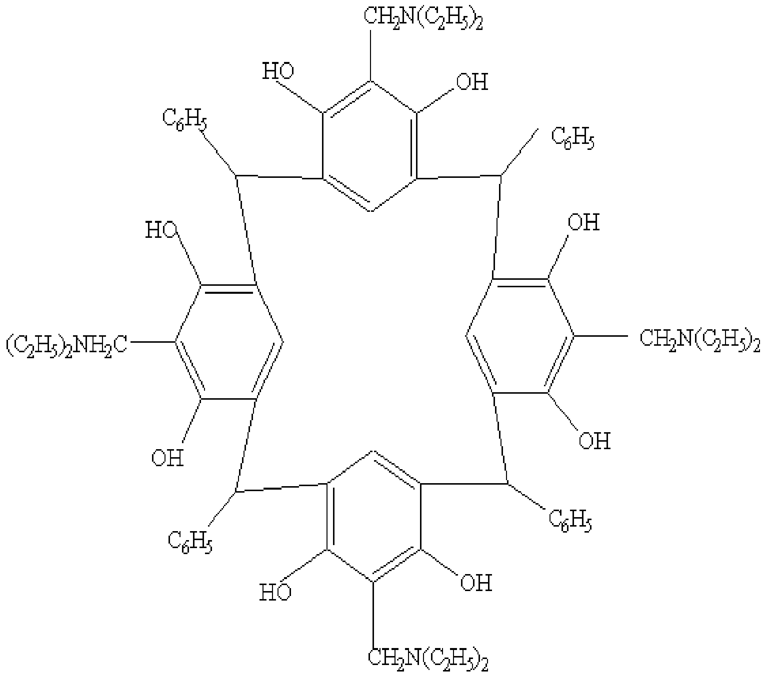


Figure 1. Chemical structure of a CBAMINE molecule.

2. Experimental details

LB films of CBAMINE were deposited by a NIMA 622 alternate LB trough with automated surface balance system. The substrates were ultrasonically cleaned microscopic glass slides for depositing process. The surface pressure is controlled using a Wilhemly plate method [7].

AFM measurement was carried out in air in tapping mode. A standard silicon nitride tip was used to obtain the 2D and 3D images and the spring constant of the cantilever was 40 nm. The AFM image was taken in an area of 4µm x 4µm. A glass slide was ultrasonically cleaned to prepared thin film and then15 layers LB films of CBAMINE were transferred onto this substrate.

Surface plasmon resonance (SPR) measurements were performed by A Kretschmann's type (BIOSUPLAR 6 Model) SPR set-up with a resolution of 0.003^0. Biosuplar-Software was used to control the SPR system settings, measurements and data acquisition as well as data presentation. The SPR data were analysed (via least squares algorithm) to obtain film thickness and refractive index using Winspall software for the theoretical fitting of the Fresnel's equations [8]. The response of CBAMINE thin films on exposures to chloroform, benzene, toluene and ethanol vapours were studied using a special a transparent plastic flow cell made in house. The reflection intensity at a constant angle of incidence was monitored as a function of time when the film remained exposed to different vapours for at least 2 minutes followed by allowing the film to recover in clean air. This process was repeated for four times to observe the reproducibility of the CBAMINE thin film as a sensing material. All organic vapour measurements were made using dry air in the small gas cell, thereby eliminating the effect of water vapour on the response properties of CBAMINE LB films [9].

3. Results and Discussion

In this study, a monolayer containing calixarene molecules has been deposited using LB film deposition technique to form multilayer sequences possessing Y-type LB deposition mode. A NIMA 622 alternate LB trough with automated surface balance was utilised to examine the molecular behaviour of CBAMINE at the air–water interface and fabricate LB film multilayer onto the different substrates. The automatically controllable barriers are employed to change molecular arrangement of the monolayers on the water surface by compressing the CBAMINE monolayer with 0.2 mm s^{-1} of barrier speed. Wilhemly plate method was employed to determine the surface pressure. By compressing the barriers, a plot of surface pressure against surface area was obtained as in figure 2.

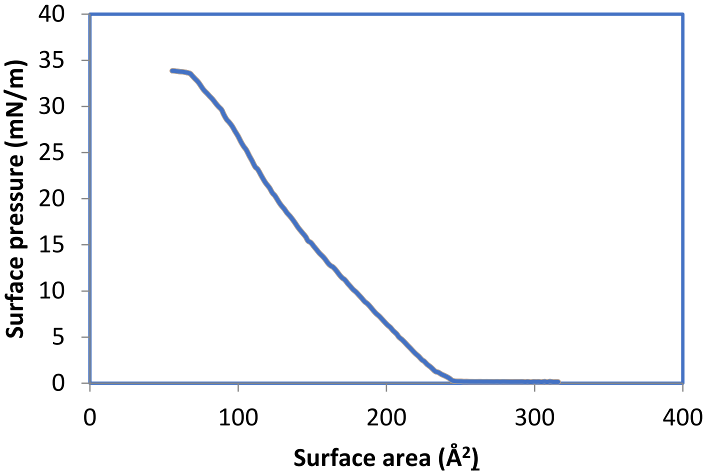


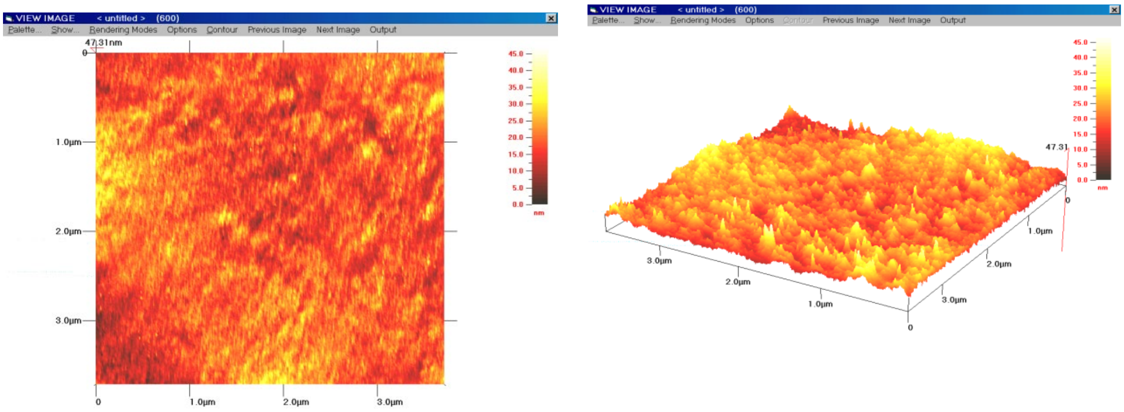
Figure 2. The pressure–area (π–A isotherm) of CBAMINE monolayer on the water surface.

By compressing the barriers, a plot of surface pressure against surface area was obtained.From the pressure–area (π–A) isotherm graph, surface pressure of the solid phase of the floating monolayer on the water surface was obtained as 20 mN/m, which are in good agreement with the reported result [10]; therefore, this surface pressure value was selected for the LB film deposition procedure.

The effectiveness of the monolayer deposition process is described by the transfer ratio (TR). A TR of close to 1.0 implies that the material exhibits good adhesion to the substrate when it is immersed in and then removed from the subphase. However, a low TR value indicates that the material does not adhere to the substrate well, and consequently, the second monolayer deposited on the film might be easily removed, resulting in a low-quality film [11]. The TR value is calculated using the following equation:

$$\tau = A_L/A_s \tag{1}$$

where A_L is the decrease in the area occupied by the molecules at the air/water interface (at solid phase) and A_S is the area of the substrate covered with the monolayer. In this study, for each monolayer, the average reduced area is calculated and the transfer ratio, τ, for a glass substrate is found to be 96 % for LB films of CBAMINE. This value can be used to conclude that steady, reproducible and uniform monolayers of calixarene molecules were deposited from the air–water interface on a glass and quarts substrates.



(a) (b)

Figure 3. (a) Two-dimensional and (b) three-dimensional AFM images of CBAMINE LB films.

Morphological examination of 15 thin layers CBAMINE molecules deposited onto an optically flat hydrophilic glass substrates were carried out using AFM tapping mode. Figure 3 demonstrates4 μm x 4 μm AFM image of LB film. Measurements were repeated using different area regions of the sample and finally seen that surface morphologies were very similar to these 2D and 3D AFM pictures. It is seen some big pairs on the surface. These bumps are supposed to be formed by the aggregation of CBAMINE molecules. These hills may be caused by irregularities of glass surface. Although the particles slightly increase the RMS value, results indicate LB films exhibited smooth, compact, uniform and void free morphology with a RMS value 4.6 nm.

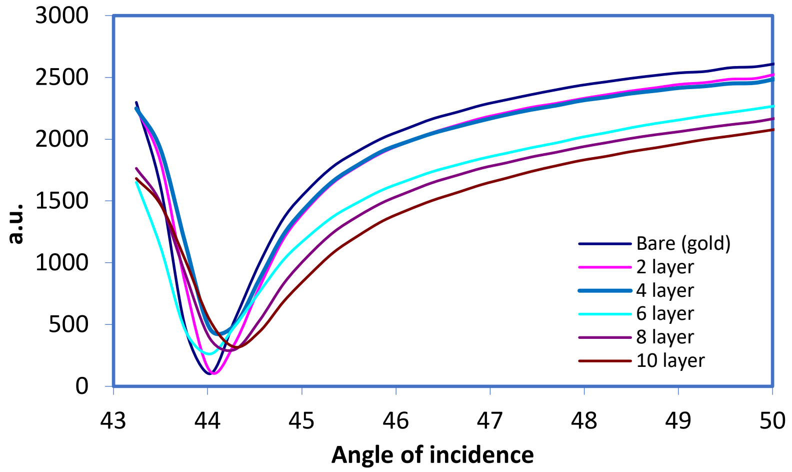


Figure 4. SPR curves of CBAMINE LB films with increase in thickness.

Optical parameters (the refractive index and the thickness) of these LB films were determined using SPR curves with a suitable fitting program (WINSPALL software developed at the Max-Plank-Institute for Polymer Research, Germany). Figure 4 illustrates SPR intensity versus angle curves for the clean gold surface, and for surfaces with deposited layers of LB films. The refractive index values ranging from 1.64 to 1.82 with a approximately thickness value of average 1.14 nm (Table1) were calculated using the fitting program. These results are good agreement with optical index and the thickness of LB films of similar calixarene based derivative [12].

Table 1. The film thickness and refractive index of the deposited LB thin films with respect to number of layers.

Number of layers	Thickness (nm)	Refractive index
2	2.0	1.48
4	4.0	1.64
6	6.4	1.72
8	8.3	1.68
10	11.3	1.90

The adsorption of chloroform, benzene, toluene and ethanol vapours was studied using SPR measurements on gold-coated glass slides with thin films of CBAMINE. The vapour remained periodically turned on and off for about 2 min and this process was repeated four times for same vapour concentration. Typical response on exposure to chloroform, benzene, toluene and ethanol vapour of four different concentrations for 10-layer LB CBAMINE film is presented in figure5. The sensor responses are reversible with recovery being achieved. For all the vapours examined, the thin film response time is fast in seconds, but the thin film response for chloroform is significantly higher when compared to the other three vapours. SPR and different other systems having layers of calixarene derivatives were used to detect chloroform vapour [13-14].

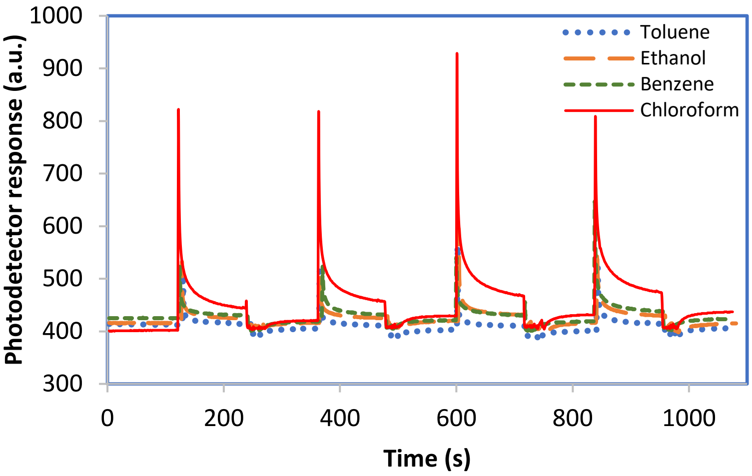


Figure 5. Effect of different VOCs on photodetector response: Toluene, ethanol, benzene, and chloroform.

4. Conclusion

We have studied gas sensing properties of CBAMINE which is calix[4]arene derivative. This molecule have been produced and deposited successfully as LB films on glass and gold-coated glass substrates. The films have been characterized morphologically and optically by means of AFM and SPR respectively. The SPR technique was also used in order to investigate the adsorption properties of CBAMINE LB films. Both steady state and in situ adsorption kinetic characteristics were obtained and LB films of this molecule were determined to be highly sensitive and selective for chloroform vapour.

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