



## Characterization of Langmuir–Blodgett films of a calix[8]arene and sensing properties towards volatile organic vapors

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### ABSTRACT

Within this article, we report the characterization and organic vapor sensing properties of Langmuir–Blodgett (LB) thin films of calix[8]arenes. Surface pressure–area isotherms show that very stable monolayers are formed at the air–water interface. The LB film could be deposited onto different substrates which allowed the films to be characterized by UV, quartz crystal microbalance (QCM), surface plasmon resonance (SPR) and atomic force microscopy (AFM). The results indicate that good quality, uniform LB films can be prepared with transfer ratios of over 0.95. QCM results showed that the deposited mass of calix[8]arene monolayer onto a quartz crystal decreased from 693 to 204 ng as the number of layers is increased. AFM studies showed a smooth, and void free surface morphology with a rms value of 1.202 nm. The sensing abilities of this LB film towards the development of room temperature organic vapor sensing devices are also studied. Responses of the LB films to various vapors are fast, large, and reversible. It was found that the obtained LB film is significantly more sensitive to chloroform than other vapors. It can be concluded that this molecule could have a potential application in the research area of room temperature vapor sensing devices.

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### 1. Introduction

Volatile organic compounds (VOCs) are organic chemical compounds which have a significant vapor pressure under ambient conditions. When released into the environment, they can contribute to global warming and also lead to soil, groundwater and air pollution within the environment [1]. VOCs are widely used in home or office environments for example within laser printers, cleaning solvents, paints, wood preservatives, carpet backing, plastics, and cosmetics. Other natural sources include trees and other plant and animal species as well as from synthetic sources such as petroleum derivatives. These vapors have been shown to contribute to several illnesses such as sick building syndrome [2], allergic sensitization [3], immune effects in infants or children or asthmatic symptoms [4], probably because concentrations of VOCs in indoor air are generally much greater than in outdoor air. Aromatic VOCs are suspected carcinogens and can potentially lead to leukemia and lymphoma upon prolonged exposure [5]. Therefore the detection of VOCs is an important issue to protect our health, wellbeing

and environment. In recent years, a significant interest in chemical sensing applications of organic materials such as carbon nanotubes [6] porphyrins [7], phthalocyanines [8] and indane [9] has been studied in order to fabricate a highly sensitive, easy to use, cheap, selective and a long life VOCs sensor. When these types of organic materials interact with VOCs, their physical, chemical or structural properties were invariably found to change, either reversibly or irreversibly, i.e., color, mass, conductivity, film thickness, refractive index changes etc.

A large area of research in the sensor application area utilizes calixarenes and their derivatives due to their multiplicity of options for targeted structural design [10–15]. The general shape of calixarenes is that of a cup with a defined upper and lower rim and a central annulus, enabling calixarenes to act as host molecules as a consequence of their preformed cavities. It is easy to modify either the upper and/or lower rims to prepare various derivatives with differing selectivities for various guest ions and small molecules [16–19]. Cage compounds such as tert-butyl-calix[n]arenes often show highly pre-organized structures with highly symmetrical cavities suitable for host–guest interactions. The resultant chemical or physical changes can be detected using a very sensitive capacitive method for the detection of solvent vapors down to a concentration of a few ppm [20]. They are also capable of binding certain

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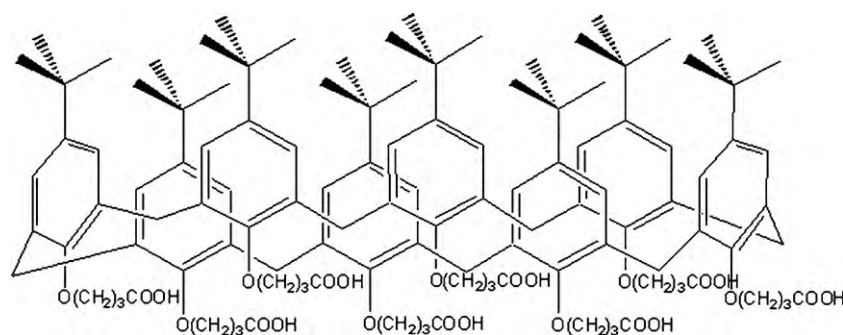


Fig. 1. The chemical formula of calix[8]acid molecule.

ions or small molecules within their cavities and for exhibiting high porosity to other species. Calix[n]arenes and their derivatives are an excellent material to organize as a monolayer on the water surface and to prepare Langmuir–Blodgett (LB) thin films [21,22]. These films have possible applications especially in the field of the environment protection such as detection of NO<sub>2</sub> [23], ozone [24], NH<sub>3</sub> or HCl gases [25], various ions [26] and various solvent vapors [20].

Calix[4]resorcinarenes have been previously incorporated into LB films and exposed to a wide range of vapors (e.g. amines, alcohols, and thiols) to study the interaction mechanism between calix and vapors. It is observed that these types of LB films are capable of binding selectively to lysine, an important amino acid [27]. Other calixarenes were deposited as thin films onto Au-coated substrates by the spin coating method. SPR measurements on these systems were utilized for the detection of benzene, toluene, ethylbenzene and *m*-xylene. Selective, fast and reversible adsorption of the vapor molecules was detected via the resultant increase in film thickness and refractive index of the spun films. The adsorption behavior of calixarenes may be explained by the capture of guest molecules in the film matrix due to the cavitated nature of the film's molecules [28].

In the present article, a calixarene containing eight phenolic groups within the macrocycle substituted with -O(CH<sub>2</sub>)<sub>3</sub>COOH side groups was selected to form LB films. Within this work we study the characterization of deposition via the LB method and utilize the resultant films as a sensing layer onto gold-coated glass. The SPR method is used to investigate the sensing properties of calix[8]arene LB films towards organic vapors such as chloroform, toluene, benzene and ethyl alcohol.

## 2. Experimental details

The chemical structure of the calix[8]arene-octa-acid is shown in Fig. 1. The calix[8]acid could be dissolved in chloroform to give a concentration of 0.25 mg ml<sup>-1</sup>. Isotherm data was measured at room temperature using a NIMA 622 type alternate layer LB trough with a Lauda Ecoline RE 204 model temperature control unit. Monolayers at a surface pressure value of 22.5 mN m<sup>-1</sup> were sequentially transferred by the vertical dipping method onto glass substrates for UV-visible and AFM measurement, onto 50-nm thick gold-coated glass substrates for SPR measurement and onto quartz substrates for QCM measurement.

The UV-visible spectra of LB film were recorded in the ultraviolet and visible spectral region from 250 to 850 nm using an Ocean Optics UV-visible light source (DH-2000-BAL Deuterium Tungsten light source) and spectrometer (USB4000) in absorbance mode. Calix[8]acid solutions in chloroform were measured in quartz cuvettes. After the deposition of LB film multilayer onto glass substrates, UV-vis spectra were recorded as a function of number of layers.

For QCM studies, calix[8]acid layers were deposited onto a thinly cut wafer of raw quartz sandwiched between two gold electrodes in an overlapping keyhole design. After each deposition cycle, the LB film sample was dried and the mass change was monitored using a home-made computer controlled QCM measurement system. Dedicated software allows the on-line recording of the changes of the quartz resonance frequency. All measurements were taken at room temperature using an in-house designed oscillating circuit and standard quartz crystals with a nominal resonance frequency of 9 MHz. The quartz crystal was inserted into the electronic control unit and the frequency of oscillation was monitored as a function of time using a computer. Values of frequency changes, which indicate the degree of response, are measured with an accuracy of 1 Hz when the organic vapor is present.

Atomic force microscopy analysis was performed using a Quanta 350 Scanning Probe Microscope. The scale is set in such a way that light colors correspond to higher structures. The images were taken using a standard silicon nitride tip (constant force 12 N/m) in the contact mode.

Surface Plasmon Resonance Spectrometer (BIOSUPLAR 6 Model) with a low power laser diode (630–670 nm) light source was employed to perform SPR measurements with an angular resolution of 0.003°. A glass prism (*n* = 1.62) is mounted within a holder so as to be available for measurement in liquid or in air environments. Glass slides with the dimensions 20 mm × 20 mm × 1 mm are coated on top by a very thin homogeneous layer of gold. A transparent plastic flow cell was made in house to be allow vapor measurements. The cell has two channels, with inlets and outlets connected to silicone tubes. Biosuplar-Software is used to control the SPR system settings, measurements and data acquisition as well as data presentation. Several modes such as single measurements, tracking mode or slope mode can be utilized and the signal displayed as a function of time. Variations within both measurement channels can be displayed in real time using this software. The photodetector response was monitored as a function of time during periodic exposure of the sample to the organic vapor for at least 2 min, this was then allowed to recover after injection of dry air. WINSPALL software developed at the Max-Planck-Institute for Polymer Research, Germany was utilized for the fitting of SPR curves to determine thickness and refractive index values of the LB films.

## 3. Result and discussion

### 3.1. Isotherm graph

Isotherm graphs of the calix[8]acid monolayers (Fig. 2) were obtained at the air–water interface by recording surface pressure as a function of surface area. These measurements were repeated several times using identical and differing volumes of the solution

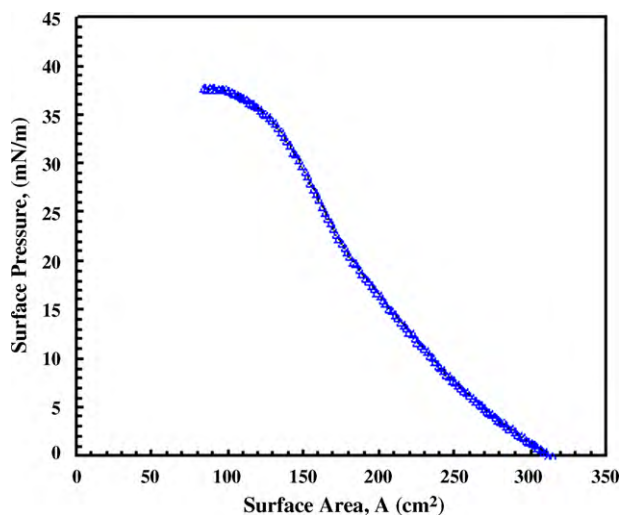


Fig. 2. Isotherm graph of calix[8]acid material.

and the results demonstrated good stability and reproducibility of the monolayers at the air–water interface.

Isotherms of calixarene compounds have been extensively studied using different materials such as calix[8]arenes [29–31] and calix[4]resorcinarenes [32,27]. When compared to our results, similar isotherms have been observed for calix[8]arene monolayers at the air–water interface. The surface pressure increased with decreasing surface area without an obvious phase transition up to  $40 \text{ mN m}^{-1}$ . The floating monolayer was found to be stable at the surface pressure value of  $22.5 \text{ mN m}^{-1}$  which is selected for LB film deposition process.

### 3.2. Deposition properties

#### 3.2.1. UV–visible results

Fig. 3 shows typical UV–vis absorption spectra of calix[8]arene molecule as a solution in chloroform and absorption band observed at 280 nm. A similar spectrum of the same compound as an LB film with different layer numbers deposited onto the quartz substrate is shown in Fig. 4. UV–vis spectra of calix[8]acid LB films exhibit slightly red-shifted absorption bands compared to the spectrum of the chloroform solution. The shift in the absorption band of the LB film may be the result of some kind of molecular aggregation which takes place during film formation, such as dimerization [33,34]. UV–vis spectra have been used to monitor the effect of

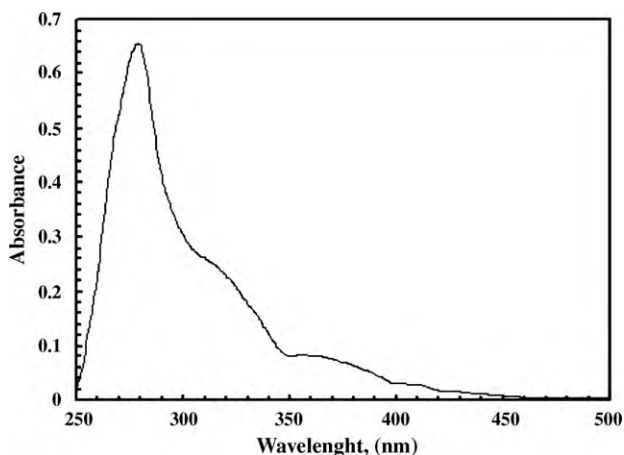


Fig. 3. The UV–visible spectra of calix[8]acid solution.

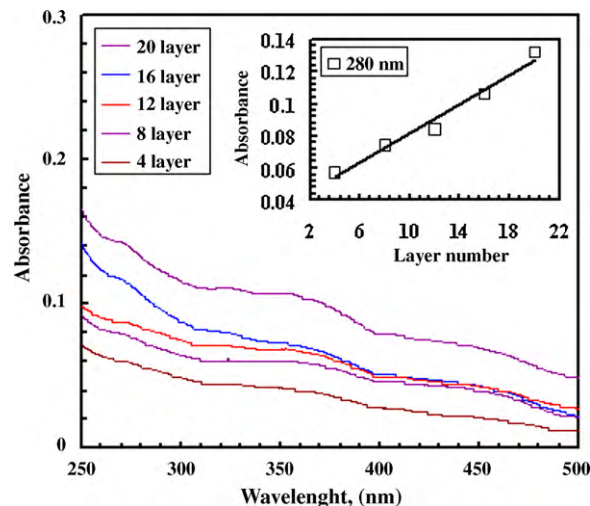


Fig. 4. UV–vis absorption of calix[8]arene LB film. Inset: linear relationship between absorbance and the number of bilayers, corresponding to the thickness of the films.

the solvent on the complexation properties between chromogenic calix[4]arene derivatives and metallic cations with extensive studies being made in solvents such as tetrahydrofuran, chloroform, methanol, acetone, ethanol, acetonitrile, dimethylformamide and dimethyl sulfoxide [35]. These results showed that the UV–vis spectra of the calixarenes are highly solvent dependent because the position, intensity and the shape of the absorbance bands of each compound in solution, have varied with changes in solvent and a red shift is commonly observed. Similar work has been found by Moreira et al. [32,36] using a calix[4]resorcinarene octafunctionalized with methyl  $\alpha$ -acetate or methyl  $\alpha$ -acetamide when deposited as LB films on several different substrates.

The UV–vis absorption spectra of multilayered films consisting of polyvinylamine (PVA) and calix[4,6 or 8]arenes have been studied to monitor transport properties using similar experimental conditions. The optical absorption spectra of these films were quite different depending on the size of calixarene rings, when the ring size increases in the ratio 4:6:8, the absorption increases in the ratio 1:2:3. It is proposed that the small rings tend to desorb more easily because the number of sulfonate groups per molecule is smaller and small and large calixarene rings generally attain different conformations [37].

The inset in Fig. 4 shows a plot of the absorbance at 280 nm of the deposited calix[8]acid LB film versus the number of LB film layers and the linear relationship confirms a fairly constant transfer ratio during sequential dipping of the slide through the LB monolayer.

#### 3.2.2. Quartz crystal microbalance results

When the surface of a quartz crystal electrode is coated with a sensitive coating, it is possible to construct a mass sensitive sensor. Therefore, QCM measurements have been widely used for the confirmation of the reproducibility of LB film multilayers using the relationship between the QCM frequency changes against the deposited mass, which should depend on the number of layers in the LB film [9,38–40]. The resonant frequency,  $\Delta f$ , of the QCM crystal for an LB film is described by:

$$\Delta f = \frac{-2f_0^2 \Delta m}{K_q} N \quad (1)$$

where  $f_0$  is the resonant frequency of the fundamental mode of the crystal (Hz),  $\Delta m$  is the mass per unit area per layer (g),  $N$  is the number of deposition layers,  $K_q = (\rho_q \mu_q)^{1/2} A$ ,  $A$  is the piezo-electrically active area ( $\text{cm}^{-2}$ ),  $\rho_q$  is the density of quartz ( $2.648 \text{ g cm}^{-3}$ ),  $\mu_q$  is the shear modulus of quartz ( $2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$ ). It is clear

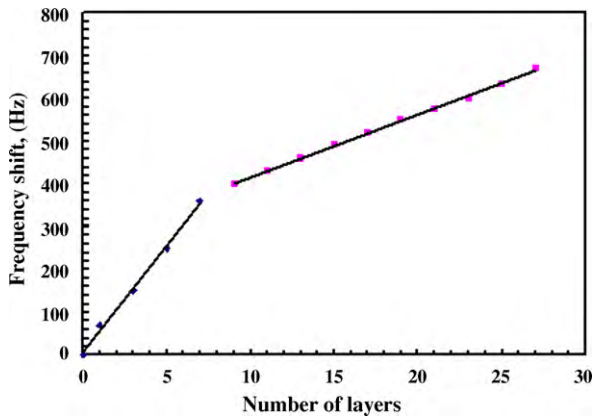


Fig. 5. Frequency changes as a function of layer numbers.

that this equation has a linear relationship between the number of layers and the change in resonant frequency for an LB film that confirms the uniform transfer process of the LB film.

Fig. 5 shows the transfer of calix[8]acid LB film onto a quartz crystal substrate. A systematic change in the frequency with the increase in the number of monolayers is clearly shown however, there are two regions observed for the change of resonant frequency. Initial changes up to seven deposited layers show a slope of 49.8 Hz and the deposited mass per monolayer is determined to be 693 ng. In the second region between 9 and 27 monolayers, the slope of graph and the deposited mass per layer decreased to 14.6 Hz and 204 ng, respectively. This decrease of deposition quality onto the quartz crystal substrate could be due to a change of the surface morphology of deposited layers. The change of frequency as a function of the number of monolayers is closely associated with the LB layer mass change, and the deposition process is strongly depend on the surface interaction between substrate and monolayer at the water–air interface.

3.2.3. Surface plasmon resonance results

To get further insight into the deposition properties of the multilayer assemblies, surface plasmon reflectivity scans were taken from calix[8]acid LB films of different thicknesses. SPR measurements were made on the LB films deposited onto gold-coated glass substrates at a lateral pressure of 22.5 mN/m. The LB monolayers were transferred uniformly onto gold-coated glass substrate with Y-type deposition. Fig. 6 displays a set of typical SPR curves

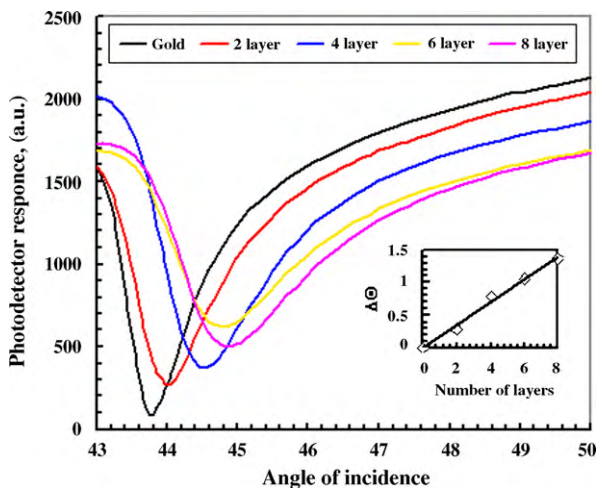


Fig. 6. SPR curves of calix[8]acid LB films with increase in thickness. Inset: linear increase of thickness as a function of number of bilayers.

showing the variations in reflected intensity as a function of incidence angle for LB films. The SPR curve for the bare gold film is also included for reference. The SPR curves of the overlayer containing the LB films become broader and the minimum reflected intensity rises to a higher value as the number of LB layers is progressively increased. Similar SPR curve changes have been observed for novel octa-substituted metal-free phthalocyanine LB films [41]. The peak shifts ( $\Delta\theta$ ) seen in the angular scans of the plasmon resonance curves of the LB film multilayer assemblies relative to bare gold, increased linearly with the number of layers. Furthermore, the observed results showed that in the case of calix[8]acid LB film, the width of the peaks broadens asymmetrically with increasing thicknesses, possibly due to an increasing surface inhomogeneity for the multilayers [42]. The multilayer thickness was found to be linearly related to the number of layers deposited, as seen by the linear increase in shift of SPR angles with the number of layers shown in the inset of Fig. 6. SPR measurements were made on several samples which reproducibly demonstrated similar characteristic features.

3.2.4. Calculation of refractive index and thickness of calix[8]acid LB film

The film thickness and refractive index of calix[8]acid layers were calculated by fitting the SPR curves with a Fresnel formula algorithm via the Winspall software. Fitting the experimental data with a theoretical model (solid curve) allows determination of the layer thickness and refractive index of the deposited LB layers. Fig. 7a illustrates SPR intensity versus angle curves for the clean gold surface, and Fig. 7b for surfaces with two deposited layers of LB films. Similar calculation was carried out using films with 4, 6,

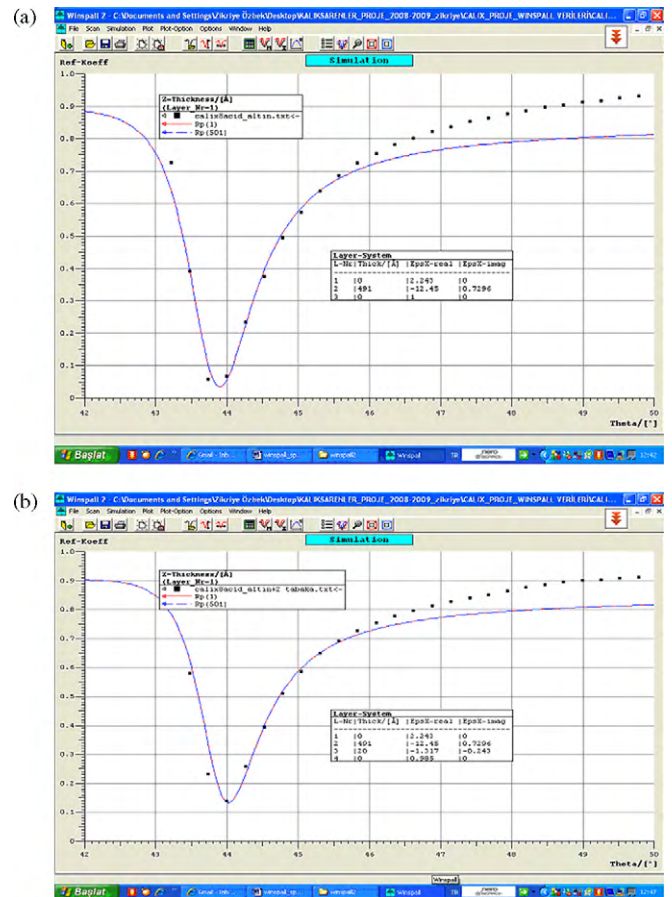


Fig. 7. (a) Complete measured (dots) and fitted (lines) SPR curves for clean gold surface and (b) complete measured (dots) and fitted (lines) SPR curves for 2 calix[8]acid LB film.

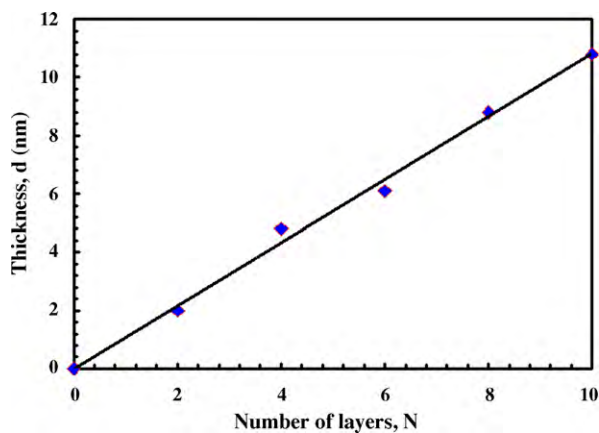


Fig. 8. Modeled layer thickness as a function of layer number for calix[8]acid LB layers. The solid line is a linear regression fit to the data ( $R^2 = 0.9947$ ).

8 and 10 layers. Fig. 8 shows that the thickness of the calix[8]acid LB films increases linearly with the number of layers, as expected for this system. The thickness of this LB film determined by the slope of the thickness versus layer number (Fig. 8) is found to be  $1.08 \pm 0.07$  nm/deposited layer with a refractive index value of  $1.21 \pm 0.08$ .

In the literature Corey–Pauling–Koltun (CPK) models were used to determine the molecular thickness of a calix[n]arene ( $n = 4$  and 8) calculated 1.5 nm [43]. X-ray studies [31] have shown that a similar calix[8]arene but with slightly different substituents has a monolayer thickness of 1.23 nm. Other work by Nabok et al. [44] utilized a calix[8]arene material to produce a LB film multilayer structure and studied the physical properties of this film by SPR and ellipsometry measurements. The thicknesses of calix LB film were determined 1.33 nm from SPR system and 1.37 nm for ellipsometry measurement. The refractive index of calix[n]arene ( $n = 4$  and 8) has been measured as 1.46 [31,45,46], 1.494 [47], 1.48 [48] and between 1.54 and 1.43 [49], respectively. Katantseva et al. [50] studied the refractive index and thickness of several calix[n]arene molecules and determined refractive indexes between  $1.47 \pm 0.01$  and  $1.70 \pm 0.01$  along with thickness values from  $0.80 \pm 0.1$  to  $1.50 \pm 0.1$  nm.

### 3.2.5. Atomic force microscopy results

Calix[n]arene derivatives can be deposited onto several solid substrates such as quartz crystal [51], mica [52], silicon [53], cadmium arachidate [54], silver [55] and ITO [56]. These studies showed that the deposition is strongly depend on the substrate surface. Root-mean-square (RMS) values for 5,11,17,23,29,35-hexaformyl-37,38,39,40,41,42-hexakis(1-*n*-octyloxy)-calix[6]arene LB film have been found to be 2.2 nm, RMS value for 4 and 8 layers of meso-octaethylcalix[4]pyrrole LB films are found to be 3.3–5.2 nm respectively. RMS values of azocalix[4]arene LB films for a  $5 \mu\text{m} \times 5 \mu\text{m}$  area on glass substrates are 0.5 nm, for a silicon substrate 0.72 nm and a ITO substrate to be 3.69 nm.

The morphological examination of calix[8]acid LB film was carried out using AFM in tapping mode. Fig. 9 depicts  $3 \mu\text{m} \times 3 \mu\text{m}$  areas of two and three dimensional AFM images of a 15 layer calix[8]acid LB film deposited at a rate of  $25 \text{ mm min}^{-1}$  onto an optically flat hydrophilic glass substrate. This measurement was repeated using different area regions of LB film sample and the surface morphologies were very similar to these AFM pictures. It is very clear that LB film exhibited a smooth, compact, uniform and void free morphology with a RMS value of 1.202 nm.

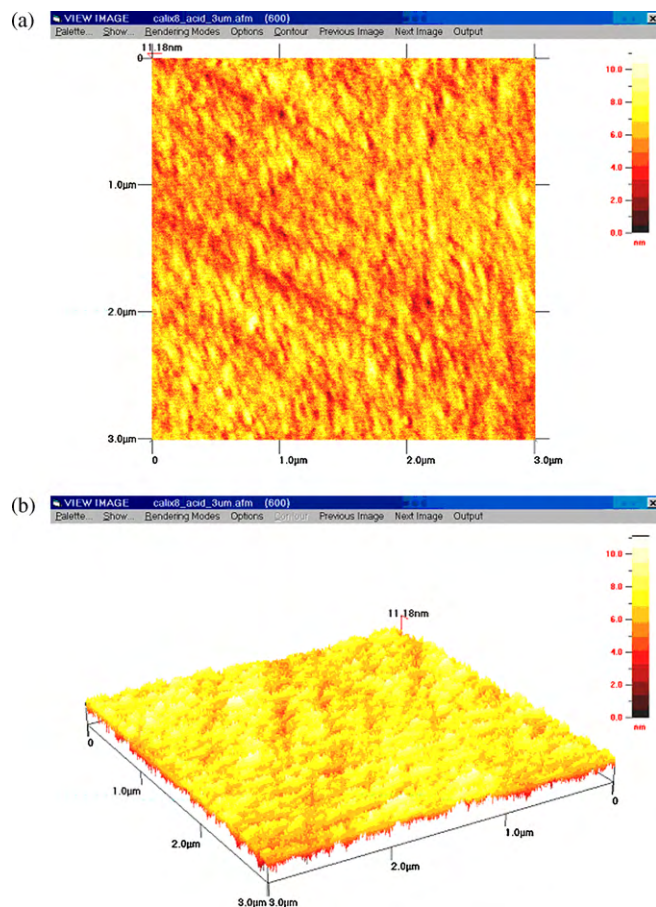


Fig. 9. (a) AFM two dimensional image for a 15-layers LB film sample and (b) AFM three dimensional image for a 15-layers LB film sample.

## 4. Sensor application

In order to study the potential application of this calix[8]acid LB film in the field of VOCs sensing, the kinetic response of the LB sample to saturated chloroform, benzene, toluene and ethyl alcohol vapors was recorded by measuring the photodetector response as

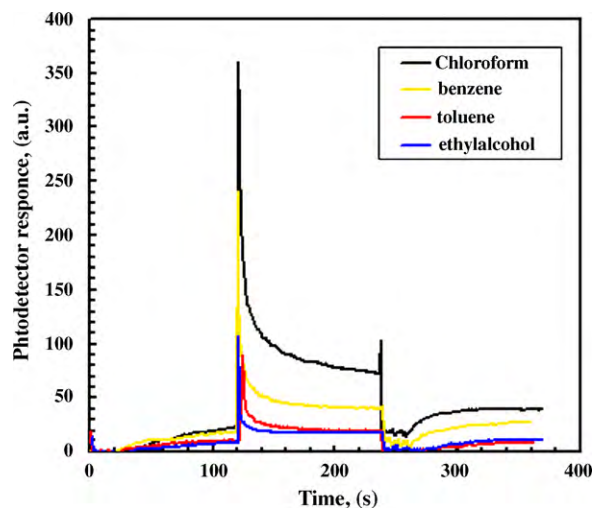


Fig. 10. Kinetic response of calix[8]acid LB film against VOCs (values for saturated vapours: chloroform 205,000 ppm, benzene 106,000 ppm, toluene 28,700 ppm, ethanol 57,700 ppm).

a function of time. The LB film sample was periodically exposed to the organic vapor for 2 min, followed by the injection of dry air for a further 2 min period. Fig. 10 shows the kinetic response of the calix[8]acid LB film to the vapors. This LB film shows a response to all vapors with a fast, reproducible and reversible response after flushing the gas cell with fresh air. The response of the LB film in the form of SPR response to saturated chloroform exposures is much larger than the other vapors with recovery times of the order of a few seconds (3 s for response and 5 s for recovery times) when the gas cell is flushed with dry air.

The adsorption mechanism of chloroform and benzene vapors has been studied for spun films of mesogenic octa-substituted phthalocyanine (Pc) derivatives [57]. Chloroform vapor interacts with phthalocyanine films predominantly by formation of hydrogen bonds between  $\text{CHCl}_3$  molecules and the alkyl chains of the Pc ring substituents and exposure to chloroform vapor was found to have more pronounced effect on the optical parameters of these film than benzene. The film thickness also increased as a result of film swelling [57]. It is clear that exposure of LB films to organic vapors yield an effect on the optical parameters such as changing the thickness and refractive index of LB film [46–48]. The sensing mechanism for calix[4]resorcinarene LB films has been studied using QCM, ellipsometry and SPR techniques. The results were interpreted in terms of capillary condensation of organic vapors in the nanoporous matrix of the calixarene LB films accompanied by film swelling of the LB films caused by adsorption leading to changes of the thickness and refractive index [46]. An amphiphilic calix[4]resorcinarene thin film was exposed to benzene, toluene, ethylbenzene, and *m*-xylene (BTEX) and showed a fast and reversible response. It was found that the refractive index of the sensing layer is changed due to the host–guest interaction between the cavitated molecules and the vapor molecules [47,48]. The response of the calix[8]acid LB films studied in this article towards chloroform can therefore be ascribed to a similar adsorption mechanism.  $\pi$ – $\pi$  interactions between benzene or toluene molecules and the calix[8]acid rings are thought to be responsible for the interaction between these two molecules, with similar interactions between benzene and phthalocyanine thin films having been demonstrated by Basova et al. [57] using the Raman spectral changes in the region of the macrocycle vibrations. The adsorption mechanism of butanol which has a dipole moment associated with the OH group, was also studied for spun films of azo-calix[4]resorcinarene (AZO) [58]. The interaction of AZO molecules with OH groups is limited, and therefore the solubility in butanol, as well as in other alcohols, is rather low. Therefore butanol exhibited the smallest response than other vapors within that system and similar results have been shown for our LB films with ethanol. Various other systems have utilized calixarene layers to detect organic vapors. Piezoelectric crystals coated with calix[4]resorcinarenes displayed very high sensitivities of a few ppm for 2-butanone but much lower sensitivities for hydrocarbons (100s of ppm) [59]. Other workers utilized an optical technique [60] to detect alcohol vapors which although it was much less sensitive (>10,000 ppm) could distinguish between different alcohols. Electrical sensors based on discontinuous gold films coated with evaporated films of calixarenes could detect water and alcohol vapors in the range 20–90% of saturated vapor concentration [61]. Quartz crystal based systems coated with spin coated films of calixarenes have been shown to be able to detect toluene and hexane at between 10–80% saturated vapor concentration [62]. Other workers used quartz crystal microbalances coated with thermally evaporated calixarenes and reported detection limits of 1000 ppm for toluene and 200 ppm for chloroform [63]. LB films and cast films have been compared for their sensitivity towards vapors [64], results showing that cast films were more sensitive although LB films gave faster response.

## 5. Conclusion

The characterization and VOCs sensing applications of thin LB film of a calix[8]acid molecule have been studied using UV–vis spectroscopy, QCM, SPR and AFM methods. Isotherm results indicated that this molecule gives a stable monolayer at the air–water interface with no phase transitions. A surface pressure value of 22.5 mN/m at solid phase is selected for the LB film deposition process which monitored using all measurement systems. A plot of UV–vis absorbance band at 280 nm as a function of number of layers gives a linear relationship proving that this material can be deposited onto the quartz substrate. Similar linear relationships that were obtained with respect to deposited mass onto quartz crystal substrate were taken for QCM measurements with two regions observed for resonant frequencies versus layer number. A fast slope change occurred for small layer numbers with a deposited mass value of 693 ng. When the number of layers increased, the deposited mass per layer decreased. According to SPR results, the LB film transfer onto a gold-coated substrate is found to be successful and monolayers were transferred uniformly onto gold-coated glass substrates. The film thickness and refractive index of calix[8]acid LB films is found to be  $1.08 \pm 0.07$  nm/deposited layer and  $1.21 \pm 0.08$ , respectively. AFM measurements demonstrated that LB films exhibited a smooth, compact, uniform and void free morphology with a rms value of 1.202 nm. A SPR system was employed to study the sensing properties of calix[8]acid LB films towards VOCs (chloroform, benzene, toluene and ethyl alcohol). The response of these LB films to saturated chloroform vapor was much larger than the other vapors and showed response and recovery times of a few seconds. It can be proposed that this sensing element deposited onto gold-coated glass substrate has an excellent sensitivity and selectivity for chloroform vapor and may find potential applications in the development of room temperature organic vapor sensing devices.

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**George A. Stanciu.** After finishing courses of Electronics Faculty from University "Politehnica" of Bucharest (1971) he worked as Engineer in R&D Institute for Electronic Components Bucharest. He joined University "Politehnica" of Bucharest in 1974, where he gained a PhD degree in Technical Physics in 1981. He became Professor of Physics in 1994. He has been working in the laser microscopy field (instrumentation and application) since 1974. In 1977 he developed the first laser scanning digital system, which was successfully used for various investigations on semiconductor materials and semiconductor devices. In 2001 he founded Center for Microscopy, Microanalysis and Information Processing in the frame of University "Politehnica" based on the research activities in Laser Scanning Microscopy and atomic force microscopy fields. He published over 150 papers (including 56 papers in internationally refereed journals) in optoelectronics field (laser radiation detectors, investigation on semiconductor lasers and photodiodes), Faraday effect, laser scanning microscopy based on OBIC techniques, confocal laser microscopy, atomic force microscopy, thin films, semiconductor quantum dots and biomaterials.

**Frank Davis** graduated from Lancaster University (UK) in 1987 and obtained his PhD at the same institution in 1991. Following postdoctoral experience at Manchester and Sheffield universities, he then spent 4 years within the battery research group at Gillette UKRDL, Reading. He joined Cranfield Health, Cranfield University (UK) in August 2002. He has a wide experience of the synthesis of calixarene type materials and novel amphiphilic and surfactant molecules. Much of his research is focussed towards the incorporation of novel sensing moieties within ultra-thin films and their use to detect a wide variety of species including organic solvents and carcinogens, as well as biological species such as ascorbate. He is the author of in excess of 80 published papers and 6 patents. He is a member of the Royal Society of Chemistry and a Chartered Chemist.