



Fabrication of Langmuir–Blodgett thin films of calix[4]arenes and their gas sensing properties: Investigation of upper rim *para* substituent effect



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ABSTRACT

This study reports the characterization and organic vapor sensing properties of Langmuir–Blodgett (LB) thin films of calix[4]arene derivatives that contain different numbers of *tert* butyl groups on their upper rims. Surface pressure–area isotherms show that very stable monolayers are formed at the air–water interface. The LB films are deposited onto different substrates, which allowed us to characterize the films by contact angle measurements, quartz crystal microbalance (QCM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The results indicate that good quality, uniform LB films can be prepared with transfer ratios of over 0.95. Meanwhile, our QCM results show that the deposition of LB film layers depends heavily on the number of *p-tert*-butyl groups and calix[4]arene with four *p-tert*-butyl groups yields the highest slope with a mass value of 1145 ng per layer. Furthermore, our AFM and SEM studies reveal a dense surface morphology for all prepared LB films. The kinetic response of calix[4]arenes containing *p-tert*-butyl groups and without *p-tert*-butyl groups as an LB film to chloroform, benzene, toluene, and ethanol vapors were investigated as a function of time. After attaching *tert*-butyl groups onto the calix[4]arene structure, the response of LB film to chloroform vapor increased. LB films of compounds **1–4** yield a response to all vapors and more often select chloroform with a larger, faster, and more reproducible response. We thus conclude that these calix[4]arenes could be applied to research concerning vapor sensing devices operating at room temperature.

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1. Introduction

It is well known that Langmuir–Blodgett (LB) thin film technique makes it possible to prepare organic, functional, ultra thin films with a controlled thickness at a molecular level and with different molecular orientations [1]. The importance of calixarenes is similarly well known and has been since the pioneering studies of Gutsche [2,3]. In short, calixarenes remain attractive to host molecules and can be easily functionalized into suitable binding sites for target guest species [4]. To briefly review, calixarenes are cyclic oligomers made of several phenolic units bounded with methylene bridges [5,6] and are regarded as the third generation of host molecules because of they are able to be included by cations,

anions, and neutral molecules [7–11]. Calix[4]arenes can be easily functionalized both at the phenolic –OH groups (of the lower rim) and, after partial removal of *tert*-butyl groups, at the *para* positions of the phenol rings (of the upper rim) [12,13]. The vast majority of these modified calixarenes exist in conical formations, each with a cavity suitable for receiving different ionic and neutral species [14]. Calixarenes are applied in enzyme mimetics, ion sensitive electrodes or sensors, selective membranes, non-linear optics, and in high-performance liquid chromatography stationary phases. Applications of calix[*n*]arenes macrocyclic host compounds in material sciences have become widespread and include mass [15], ion [16] and optical [17] sensors, non-linear optics, molecular tectons [18] in crystal engineering, and LB films for gas separation [19]. Because of the structural characteristics and stability of calixarene, the LB technique [20] has frequently been used in calixarene studies. Functionalized amphiphilic calixarenes have been prepared so that their monolayers, LB films, and self-assembly films may be further examined [21]. This is due to the fact that the LB thin film technique is a useful way of forming sequential layers

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of ultrathin organic films [22] and can precisely control the thickness and order of a film at the molecular scale [23]. Calixarene and their derivatives can be used as specific ligands for analytical chemistry, sensor techniques, medical diagnostics, and during material synthesis [24]. Different types of calixarene sensors have been widely reported in the literature. Optical sensors based on calixarenes have been designed to detect various metal ions [24–30], gaseous ammonia [31,32] and organic amines [33]. Piezoelectric quartz crystal calixarene sensors have been designed to monitor volatile organic pollutants in the gas phase, as well as in aqueous solution [34–37]. Additionally, the calix[*n*]arene cavities have proven to work well as sensitive materials in bulk layers not only for the detection of volatile organic compounds, such as halogenated and aromatic hydrocarbons [38], as well as in monolayers [39], but also for the electrochemical detection of ions [40]. Developments in gas sensing technology have become a serious aspect to consider because the need to control air quality has become an environmentally important issue. Improving the performance of the gas sensing devices mostly depends on the sensitivity and selectivity of the sensing materials. Regarding gas sensing, the use of organic materials has increased because of their simple, low cost synthesis, as well as their wide range of physical and chemical properties that can be tailored by changing their compositions. Recently, calix[*n*]arenes and their derivatives have been extensively studied for their possible application to sensors and electronic devices, for they can be highly selective molecular receptors for various metal ions and organic compounds, which allows their use in various separation and analysis applications [41,42]. The host–guest interaction is often a dynamic process in which adsorption and desorption of vapor molecules occurs when a sensing element is exposed to vapors. It is well known that when a gas molecule is adsorbed onto the surface of an organic material, the physico-chemical properties, including the structural, electrical, and optical properties, of this sensing material can change. It is important to understand the mechanism of interaction between the sensing element and the organic vapors for the design and synthesis of new molecules to detect and identify organic vapors at low concentration. The chief difficulty in gas identification continues to be the fabrication of stable sensors with a high sensitivity and selectivity toward the substance to be detected. Several measurement techniques, such as surface plasmon resonance (SPR), UV–vis and quartz crystal microbalance (QCM), are used to detect and monitor various gases because of their array of potential applications. One example is environmental monitoring, such as detecting the presence and concentration of toxic or otherwise dangerous gases that are released through spillage or leakage [43].

In this study, the preparation of LB films of calixarene derivatives contain four (1), three (2), two (3) and no (4) *p*-*tert*-butyl groups on the calix[4]arene upper rims (Fig. 1) was evaluated at the air/water (A/W) interface using isotherm graphs. Investigations of the composition and structural organization of films on glass substrate were performed by contact angle (CA), atomic force microscopy (AFM) and scanning electron microscopy (SEM). A QCM system was implemented to demonstrate the thin film deposition on a quartz crystal substrate. This method was also employed to investigate the *para* substituent effects of calix[4]arene compounds (1–4) of LB films on organic vapors such as benzene, chloroform, toluene, and ethanol.

2. Experimental details

2.1. Materials

High purity water (18.2 M Ω cm) that had been passed through a Millipore Milli-Q Plus water purification system was used to prepare water subphase mixture. The glass substrates were

purchased from Fisher Scientific. Chloroform (extra pure, Merck) was employed as spreading solvent. Benzene, toluene and ethanol were supplied from Aldrich. All materials were used without further purification. Starting calixarene compounds 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (1), 5,11,17-tri-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (2), 5,17-di-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (3), 25,26,27,28-tetrahydroxycalix[4]arene (4) were synthesized according to previously published procedure [6,9,11].

2.2. Synthesis of calix[4]arene compounds

Although compound 1 is commercially available, we synthesized our own in our laboratory to obtain a sample of higher purity. The *p*-*tert*-butyl calix[4]arene was *deterbutylated* by using AlCl₃ and phenol in toluene to produce compound 4. To obtain selective *deterbutylated* calix[4]arene derivatives 2 and 3, firstly compound 1 was interacted with benzoyl chloride in the presence of *N*-methyl imidazole in toluene for compound 2. The product was then *deterbutylated* with AlCl₃ in toluene at room temperature. Finally, the three ester functions were hydrolyzed with NaOH in a water/ethanol medium. The resulting compound 2 was obtained in a 90% yield as a white solid [44]. Compound 2 was easily synthesized from compound 1 and benzoyl chloride using MeCN as solvent and K₂CO₃ as base. The subsequent Friedel–Crafts *deterbutylation* step was carried out in toluene using AlCl₃, and the two benzoate groups were then removed in alcoholic NaOH at reflux. The compound 4 was thus obtained in an almost quantitative yield as a white solid [45]. All of the structures have been characterized through ¹H NMR, FTIR (ATR), and elemental analyses. In the solution, all of the structures appeared in conical conformation as proven by the appearance of ArCH₂Ar, which displays a typical AB type proton signal at 3.20–4.20 ppm (*J* = 13.1–13.3 Hz).

2.3. Deposition of LB films

A NIMA 622 alternate LB trough with automated surface balance was used to investigate the behavior of the molecules at A/W and fabricate LB film multilayer onto glass substrates. Before each experiment, barriers and the Teflon trough of the LB film system were rinsed with ultrapure water after being cleaned with ethanol. The surface pressure was measured by using a Wilhelmy balance, equipped with a strip of chromatography paper suspending at the A/W interface. The temperature of the water subphase was controlled using a Lauda Ecoline RE204 model temperature control unit and all experimental data were taken at 20 °C. Calix[4]arene molecules were dissolved in chloroform with a concentration of 1 mg mL⁻¹ and were subsequently spread onto ultrapure water subphase at pH 6. Solutions were spread by a Hamilton microliter syringe onto the subphase solution by distributing the droplets over the entire trough area at 20 °C. A time period of 15 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. The pressure–area (π –*A*) isotherm graph given in Fig. 2 was determined with the accuracy of 0.1 mN m⁻¹. (π –*A*) graphs of calix[4]arene molecules were recorded as a function of surface area using the compression speed of barriers at a value of 172 mm² min⁻¹.

As shown in Fig. 2, an extrapolation of the linear part produces the values of area per molecule in the condensed state (1.71 nm², 1.21 nm², 1.19 nm² and 0.75 nm² for compounds 1, 2, 3, and 4, respectively). It is clear that the area per molecule depends on the number of *p*-*tert*-butyl groups or molecular weight. It should be noted that the expected approximate area per molecule for the calix[*n*]resorcinarene unit is in the range 1–2 nm² reported for similarly sized calixarenes with different side chains [46–48]. The area per molecule values found in this work closely agree with

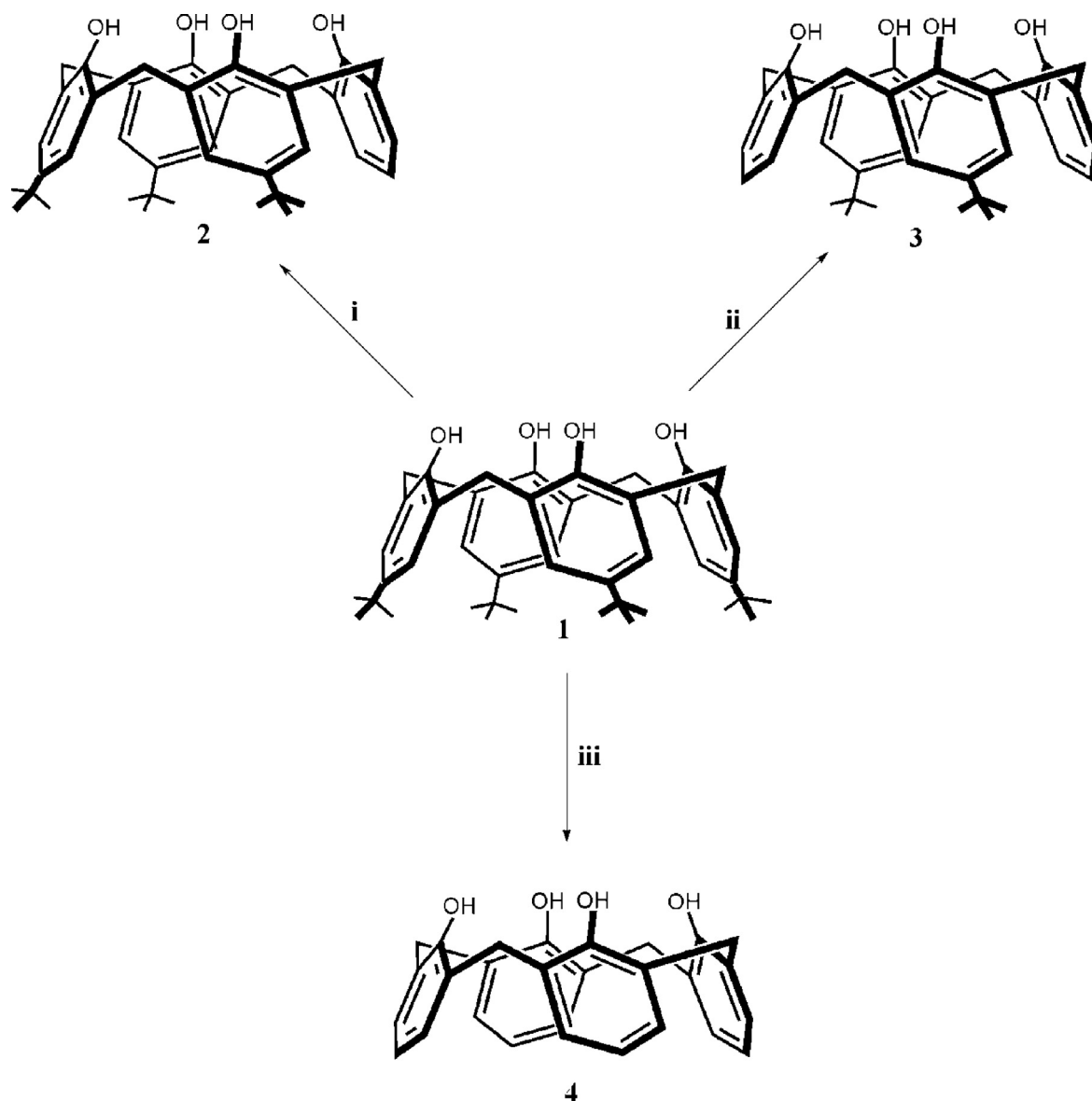


Fig. 1. Chemical structures of calix[4]arene molecules used for Langmuir–Blodgett films. (i) Benzyl chloride, *N*-methylimidazole, AlCl_3 , NaOH; (ii) Benzyl chloride, K_2CO_3 , AlCl_3 , NaOH; (iii) AlCl_3 , phenol, toluene, rt, 1 h.

the reported values of 1.16 nm^2 [49], $1.1\text{--}1.6 \text{ nm}^2$ [50], 1.02 nm^2 [51]. Area per molecule values of 1.1 nm^2 and 0.75 nm^2 are found for two calix molecules. The value of 1.1 nm^2 for calix 1 molecule suggests that a monolayer is formed at A/W interface. The corresponding value for calix 2 is 0.75 nm^2 , which suggests that this calix[4]resorcinarene aggregates in the spreading solution to a greater extent than that of calix 1 [52].

Monolayers of calix[4]arene molecules at the water's surface were found to be stable. Surface pressures of 20 mN m^{-1} were selected for LB film deposition on the glass substrates for QCM measurements. Y-type LB deposition mode and a vertical dipping procedure was performed at the selected surface pressure with a speed of 10 mm min^{-1} for both the down and up strokes. LB film samples were dried for 5 min after each up stroke.

The deposition efficiency of the LB films is denoted by the transfer ratio τ , which is the ratio of the area of the monolayer removed from the air–water interface during deposition to the area of substrate to be deposited. τ is given by:

$$\tau = \frac{A_L}{A_S} \quad (1)$$

where A_L is the decrease in the area occupied by the monolayer on the water surface, while A_S is the coated area of the substrate. Using Eq. (1), τ is found to be 0.95.

2.4. QCM measurements

A block diagram of our home made QCM measurement system is shown in Fig. 3. A thinly AT cut quartz crystal sandwiched between two electrodes in an overlapping keyhole design was used for QCM measurements. These QCM crystals with a nominal resonance frequency of 3.5 MHz were commercialized from GTE SYLVANIA company. All measurements were taken at room temperature (20°C) using an oscillating circuit that we designed. The quartz crystal was inserted into the electronic control unit, and the frequency of oscillation was monitored as a function of time using dedicated software. The values of frequency changes, which indicate the degree of response, are measured with an accuracy of 1 Hz. After each deposition cycle, the LB film sample was dried for half an hour and the mass change was monitored using this computer controlled QCM measurement system. This system was used for

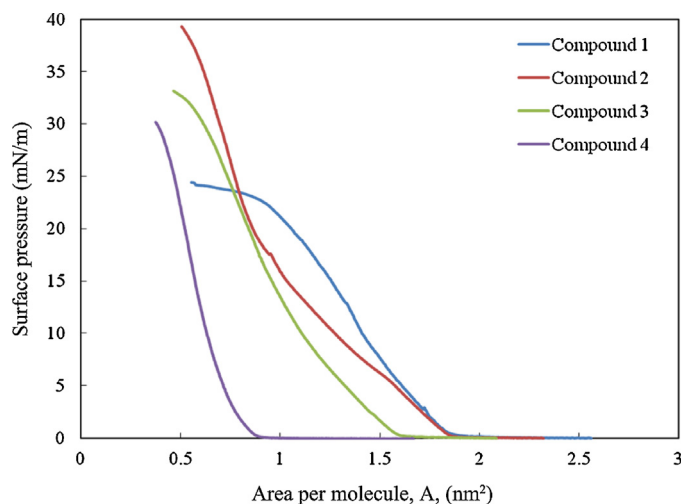


Fig. 2. π - A isotherm graph of all calix[4]arene LB films. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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.

A special gas cell was constructed to study the kinetic response of calix LB films on exposure to organic vapors by measuring the frequency changes. These measurements were performed with a syringe. The variation of the QCM frequency was monitored as a function of time when the sample was periodically exposed to the organic vapors for at least 2 min and was then allowed to recover after the injection of dry air. This procedure was carried out during several cycles to observe the reproducibility of the LB film sensing element.

All organic vapor measurements were taken in dry air condition in a small gas cell which could eliminate the effect of water vapor on the response properties of calix[4]arene LB films. In the literature calix[4]arene molecules are used to study the

water vapor effect as a humidity sensor because they are macrocyclic molecules that they can be easily functionalize from their upper and lower rims. Humidity sensing properties of calix[4]arene films includes both carboxylate and sulphonate groups are sensitive to water vapor molecules. This water soluble calix[4]arene film swelled due to water uptake and can be used as a humidity sensor [53]. Another study was carried out for humidity sensing behavior using the calix[4]arene and 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (THBC) thin films [54]. The results suggested that the -OH groups are protected by being buried in the cavities of the molecules. This may explain why the calix[4]arenes were highly hydrophobic, and the interaction between water and calix[4]arene was weak. Therefore, THBC thin film was more sensitive to humidity than was calix[4]arene. In our study calix[4]arene derivatives have not carboxylate and sulphonate groups which are sensitive to water molecules. On the other hand, our wetting measurement results indicated that our calix[4]arene molecules have more hydrophobic behavior (around 70°) than hydrophilic behavior. As a result of these we believed that the water vapor effect in our experimental conditions is minimized and can be negligible. Therefore the effect of water vapor on the response properties is not measured or studied in this work.

3. Results and discussion

3.1. Contact angle results

We measured the contact angle as an indirect confirmation of the coating of the molecules on the glass surface. The contact angle is very sensitive quantitative indicator of the wettability of the calix[4]arene films. The water drop contact angle on bare glass surface depends significantly on the surface pretreatment and can vary between 3° and 15° . For our glass surfaces, the equilibrium contact angle of Milli-Q water on cleaned and activated glass surface was measured to be $3.2^\circ \pm 0.9^\circ$, while the equilibrium contact angle for the glass coated with the calix[4]arenes containing tetrabutyl, tributyl, and dibutyl and without butyl groups were $83.7^\circ \pm 2.5^\circ$, $75.3^\circ \pm 0.6^\circ$, $71.4^\circ \pm 2.1^\circ$ and $67.0^\circ \pm 1.5^\circ$, respectively. The contact angle changes marginally as the calix[4]arene coated surfaces turn

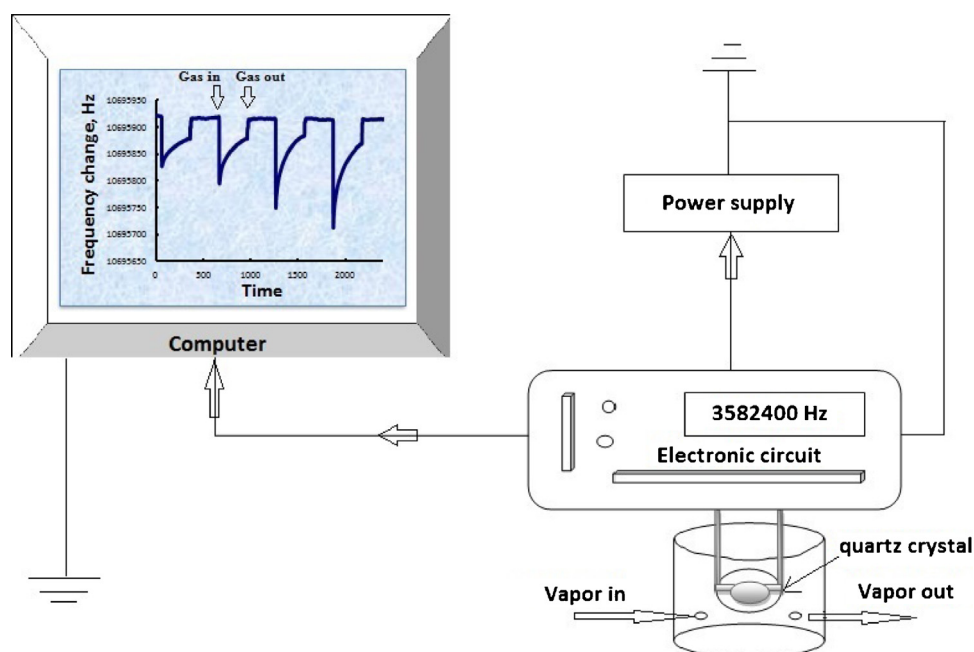


Fig. 3. A block diagram of the quartz crystal microbalance measurement system.

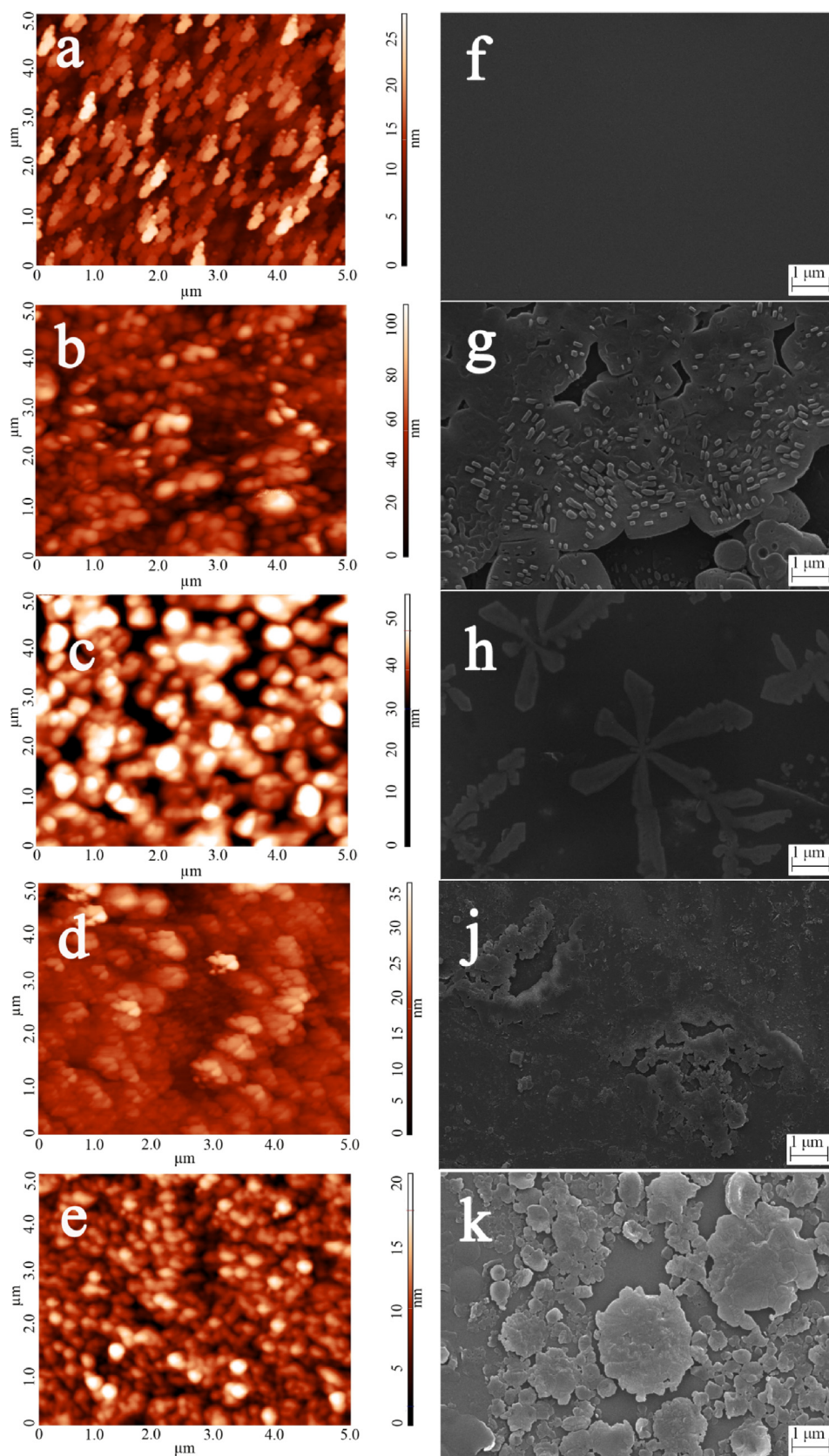


Fig. 4. AFM (left side) and SEM (right side) images of Langmuir–Blodgett films substrates: (a) and (f) bare glass surface, (b) and (g) calix[4]arene compound **1**, (c) and (h) calix[4]arene compound **2**, (d) and (i) calix[4]arene compound **3**, (e) and (j) calix[4]arene compound **4**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

more hydrophilic due to the decreasing tertiary groups (see Supplementary data for more information).

3.2. AFM and SEM analysis

Fig. 4 presents the topographic images of the surfaces of an active glass surface and the glass surface coated with calix[4]arene molecules. The AFM image of the active glass surface (Fig. 4a) consists of grainy structures in certain areas; otherwise, it is flat with an area roughness of 2.00 nm and a root-mean-square (rms) roughness of 2.95 nm on a $5 \times 5 \mu\text{m}$ scale. Fig. 4(b)–(e) shows the surface topographies of the calix[4]arene multilayers with decreasing tertiary alkyl groups located on the lower rim onto the glass surface, which are significantly different from the topography in Fig. 4(a). This result suggests that, the formation of calix[4]arene films changed the topography of the glass surface. Their average roughness and root mean square values are 13.02 nm, 16.59 nm; 4.53 nm, 6.11 nm; 3.24 nm, 4.09 nm and 2.38 nm, 3.05 nm for LB films of compound 1, compound 2, compound 3 and compound 4, respectively. It can be seen that the calix[4]arene films on the glass surface are uniform, dense, and homogeneous with some surface aggregates.

The SEM image of the clean glass substrate shows a flat and rough surface (Fig. 4f). The SEM image of calix[4]arene LB film contains four tertiary alkyl groups, shows some globular units with few aggregates (Fig. 4g). The SEM image of calix[4]arene LB film contains three tertiary alkyl groups, shows a dense form, and resembles flower-like bodies (Fig. 4h). The SEM image of calix[4]arene LB film contains two tertiary groups showing a cluster formation and not so compact structured film (Fig. 4i). Fig. 4j shows that calix[4]arene LB film contains no tertiary groups accumulated cluster-like bodies as well as more compact, homogeneous globular units.

3.3. QCM measurements

QCM measurement technique is widely applied to monitor the deposition quality of thin films on a quartz crystal substrate because the resonant frequency, Δf , is extremely sensitive to a small mass change given by [55]

$$\Delta f = \frac{-2f_0^2 \Delta m}{\rho_q^{1/2} \mu^{1/2} A} \quad (2)$$

where f_0 is the initial frequency of the crystal (Hz), Δm is the mass change (g), A is the piezo-electrically active area (0.785 cm^2), ρ_q is the density of quartz (2.648 g cm^{-3}), and μ_q is the shear modulus of quartz ($2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$).

The QCM measurements can confirm the reproducibility of LB film multilayers transfer using the relationship between the QCM frequency changes against the deposited mass. For an LB film, Δf should be directly related to the layer number and the change in resonant frequency given by:

$$\Delta f = \left(-\frac{2f_0^2 \Delta m}{\rho_q^{1/2} \mu^{1/2} A} \right) N \quad (3)$$

where N is the number of layers and, Δm is the mass per deposited layer. When Eq. (3) is rearranged, the mass change can be described as:

$$\Delta m = -\frac{\Delta f \rho_q^{1/2} \mu^{1/2} A}{2f_0^2 N} \quad (4)$$

if the numerical values in Eq. (4) are arranged as

$$\Delta m = -\frac{\Delta f (2.648)^{1/2} (2.947 \times 10^{11})^{1/2} (0.785)}{2(3582400)^2 N} \quad (5)$$

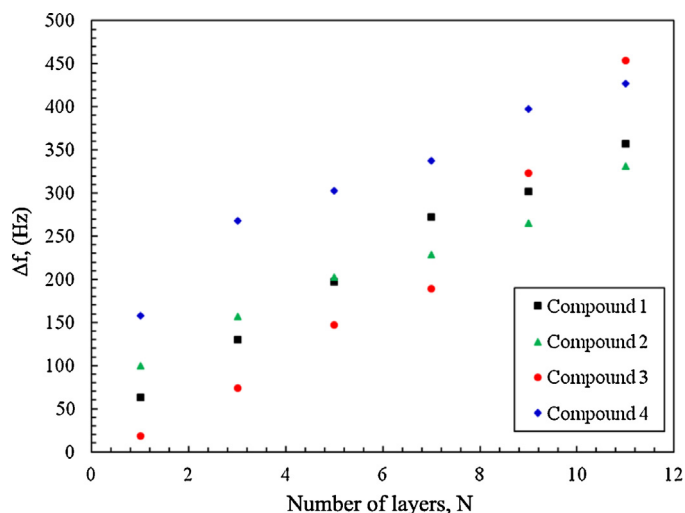


Fig. 5. Frequency shift as a number of layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Finally, the change in resonant frequency for our LB films is given by

$$\Delta m = 27 \times 10^{-8} \left(\frac{\Delta f}{N} \right) \quad (6)$$

This equation clearly indicates that a linear relationship between the mass of the number of layers and the change in resonant frequency for LB films confirms the uniform transfer process of the LB film.

Fig. 5 depicts the transfer of calix[4]arene LB films on a quartz crystal. A systematic change in the frequency with an increase in the number of monolayer is clearly observed. The change in frequency as a function of the number of monolayer is closely associated with the LB layer mass change. Furthermore, the process was shown to be reproducible. This is a linear dependence change that reveals the uniform transfer of calix[4]arene LB films and this suggesting that the equal mass per unit area is deposited onto the quartz crystal during the transfer of LB film layers.

The frequency shift per layer ($\Delta f/N$) of calix[4]arene LB films are determined from the slope shown in Fig. 5. $\Delta f/N$ and the mass deposited on the active area of the quartz crystal are presented in Table 1. Similar results indicate that the increasing surface pressure increases the amount of deposited mass [56].

As reported in Table 1, the deposition of LB film layers depends heavily on the number of *p*-*tert*-butyl groups. The highest slope is given by compound 3, which contains two *tert*-butyl groups. The second highest slope is taken from compound 1 with four *tert*-butyl groups. There is not an apparent relationship between the molecular weight of the molecules and the frequency shift due to the first layer. This result could derive from a different macromolecular aggregation that depends on the interplay among the conjugated molecules, the solvent, and the substrate surface [57].

It is important to understand the mechanism of interaction between the sensing element and the organic vapors for the design and synthesis of new molecules to detect and identify organic

Table 1
Frequency shift per layer of QCM results and deposited mass values.

LB film	$\Delta f/N$ (Hz layer ⁻¹)	Δm (ng)
Compound 1	29.44	795
Compound 2	21.5	581
Compound 3	42.41	1145
Compound 4	25.28	683

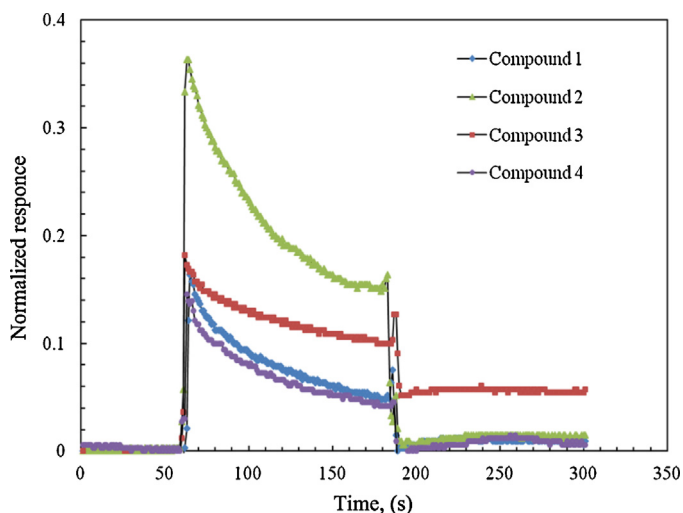


Fig. 6. The response of chloroform vapors to all LB films. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

vapors. The host–guest interaction is often a dynamic process where adsorption and desorption of vapor molecules will occur when a sensing element is exposed to vapors. It is widely known that when a gas molecule is adsorbed onto the surface of an organic material, the physicochemical properties, including the structural, electrical, optical, and mass properties, of this sensing material can change. In the literature, there are many studies on vapor sensing properties of calix[*n*]arene with several substituted groups containing LB thin films. Calixarene LB films consist of a nanoporous matrix formed by the intrinsic calixarene cavities, as well as by the gaps between the molecules and between the substituent alkyl chains. Organic vapors can penetrate through these pores inside the film matrix and condense there [58]. The kinetic response of calix[4]arene containing *p*-*tert*-butyl group as an LB film to chloroform, benzene, toluene, and ethanol vapors was examined. In order to determine the frequency change of the organic vapor, the response of an uncoated QCM crystal and a LB film coated QCM crystal was investigated in our previous study for the calibration of our system. It is thus concluded that the response of an uncoated QCM crystal is smaller than that of the LB film coated QCM crystal, which is insignificant [59].

Using QCM measurement technique the resonance frequency was recorded as a function of time. Fig. 6 shows the normalized response as a function of time when the sample was periodically exposed to chloroform vapor with a concentration value of 2.78×10^8 ppm for 2 min and followed with an injection of dry air for another 2 min period. The concentration values of organic vapor (see Table 2) in ppm are calculated by the formula as follows [60]:

$$c = \frac{\rho V (22.4 \text{ L/mol}) 10^6}{M V_0} \quad (7)$$

$$c = \frac{22.4 \times \rho V \times 10^6}{M V_0} \quad (8)$$

where c (ppm) is the concentration of vapor, ρ (g mL^{-1}) is the density of vapor, V (mL) is the volume of vapor which is injected into the gas chamber, M (g mol^{-1}) is the vapor molecular weight, and V_0 is the volume of the gas chamber (~ 0.002 L). The vapor volume values are used in this study in the following order: 20% for $V = 2$ mL, 40% for $V = 4$ mL, 60% for $V = 6$ mL, 80% for $V = 8$ mL, and 100% for $V = 10$ mL.

The normalized response described in Eq. (9) is calculated as the difference between the observed frequency response (f) and

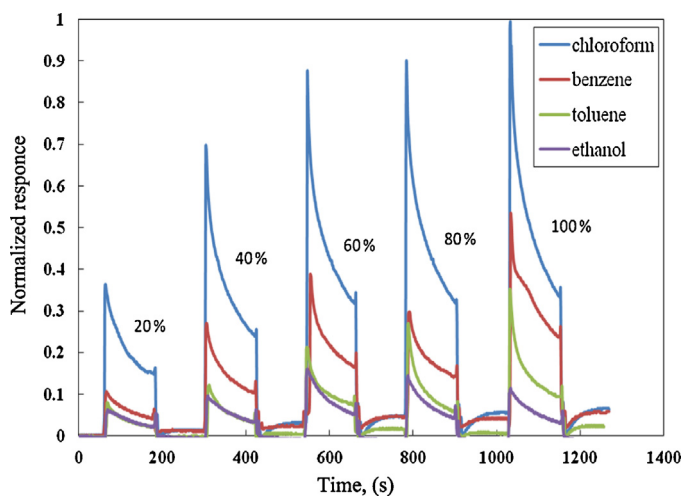


Fig. 7. Kinetic measurements of compound 2 LB film with increasing concentration of vapors as a function of time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the baseline frequency response (f_0). The resultant quantity is then divided by the baseline frequency response.

$$\text{Normalized response} = \left(\frac{f - f_0}{f_0} \right) \quad (9)$$

The values of Δf [$\Delta f = (f - f_0)$], which indicate the degree of response, are measured with an accuracy of 1 Hz. It is very clear that all calix[4]arene molecules yield a fast response to chloroform vapor. The highest response is taken using compound 2, while compound 3 gives a response smaller than that of compound 2. Compound 1 and 4 give almost the same response. The mechanisms of interaction among organic vapors in an LB film structures can be explained by three steps: the processes of surface adsorption, diffusion, and desorption. The surface adsorption effect between LB film structure and vapor molecules causes sharp frequency change when LB film is introduced with organic vapors [61]. After this interaction, the increase in frequency slows due to the bulk diffusion effect, which is also called dynamic process. When the number of adsorbed and desorbed molecules is equal, the frequency shift achieves the stable value until the dry air is flushed into the cell. The frequency change is directly proportional to the number of adsorbed vapor molecules. It can be thus concluded that the adsorption of vapor molecules is easier onto the LB film structure using compound 2 than all others. When the vapor molecules were removed from the gas cell, only desorption process occurs and the frequency change decreases rapidly. In order to investigate LB film sensing properties regarding other organic vapors, the compound 2 LB film was selected. QCM frequency was measured at the first 2 min in air, and following another 2 min period, organic vapor was introduced into the gas cell. After this procedure, dry air was injected into the gas cell to check the recovery of the sensing material. This kinetic measurement was carried out during 5 cycles with increasing concentrations to observe the reproducibility of the compound 2 LB film. Fig. 7 shows the kinetic response of the compound 2 LB film in the form of frequency change to all vapors. They are almost reversible with response and recovery times reported by Table 3 in the order of a few seconds when the gas cell is flushed with dry air. For a reproducible LB film gas sensor, sensing material should always give the same pattern of the output signal when the sensor is repeatedly exposed to an organic vapor at constant intervals of time. It is clear that compound 2 yielded a relatively stable repeatability, a good reproducibility, and almost uniform changes in frequency due to the adsorption and desorption processes.

Table 2
The concentration values of organic vapors.

Organic vapors	ρ (g cm ⁻³)	M (g mol ⁻¹)	c (20%) $\times 10^8$ ppm	c (40%) $\times 10^8$ ppm	c (60%) $\times 10^8$ ppm	c (80%) $\times 10^8$ ppm	c (100%) $\times 10^8$ ppm
Chloroform	1.483	119.38	2.78	5.56	8.34	11.12	13.90
Benzene	0.876	78.11	2.51	5.02	7.53	10.04	12.55
Toluene	0.870	92.14	2.11	4.22	6.33	8.44	10.55
Ethanol	0.789	46.11	3.83	7.66	11.49	15.32	19.15

These results show that the compound **2** LB film yields a response to all vapors and is more selective to chloroform based on a host–guest recognition mechanism with CH₂– π interaction [62]. The response of compound **2** LB film to chloroform exposures is quite large, fast, and reproducible. Upon removing the chloroform vapor, the compound **2** LB film recovery was similarly faster than others.

The value of the vapor response is proportional to the changes in frequency of the QCM measurements. It can be seen that its response to all vapors is very fast and reversible. Such behavior of sensors can be explained by the interaction between the chemical structure of material and the organic vapor. The Δf in QCM generally increases with the molecular weight of organic vapors, while the sensitivity of the film depends on the molecular weight and structure of the analyte molecules adsorbed onto the film surface. For the interaction mechanisms, it was proposed that the frequency response during adsorption is either due to dipole/dipole or a hydrogen bonding interaction [63]. It is reasonable to assume that if the number of adsorbed molecules on an adsorbent is limited and identical for various adsorbents, a greater molar mass of adsorbent would lead to a larger frequency shift. As shown in Fig. 7, the response of calix[4]arene LB film for the organic vapors at various concentration values given in Table 3 (20%, 40%, 60%, 80%, and 100%) are in the following ascending order: ethanol < toluene < benzene < chloroform. The Δf in QCM generally increases with molecular weight of organic vapors; however, the molecular weight of benzene is lower than that of toluene vapor. It is well known that Δf is directly proportional to the number of adsorbed vapor molecules. This result can be summarized that the number of adsorbed benzene vapors is higher than toluene vapors because benzene has a lower molar volume and a relatively high viscosity parameter, which indicates that benzene molecules are more mobile than the toluene vapors and penetrate easily into the calix[4]arene LB film structure [64].

A comparison of the LB film of compounds **1** to **4**, the calixarene derivatives, especially contains *tert*-butyl groups, reports better results for organic vapors. The cavity of the calixarene with *tert* butyl groups is large enough to include organic molecules. This situation agrees with the results of related literature because the structural changes in the calixarene scaffold, such as removing the *para* substituents affect the molecular interactions [65]. Generally, removing *tert* butyl groups at the *para* position significantly decreased the molecular interaction of calixarenes. In this study, however, excellent experimental results were observed for compound **2** containing three *p*-*tert*-butyl groups on the upper rim of the calix[4]arene scaffold. This situation probably results from there being one aryl group of calixarene skeleton, which is rotated upward to produce the partially conical conformation [66]. This

formation may also affect the gas sensing efficiency of compound **2** toward organic vapors.

4. Conclusion

This study investigated the characterization and organic vapor sensing properties of LB thin films of calix[4]arene derivatives containing different number of *tert*-butyl groups on the upper rim. They are very ordered at the A/W interface as an LB monolayer, which is transferred at several substrates with transfer ratios of over 0.95. QCM results are used to calculate the deposited mass values, which depending heavily on the number of *p*-*tert*-butyl groups. Using wettability measurements, the contact angle was determined as the average value of measurements in five neighboring sites of film, while LB film modified with pure component calix[4]arenes with tetrabutyl, tributyl, and dibutyl and without butyl groups on upper rim calixarene skeleton were $83.7^\circ \pm 2.5^\circ$, $75.3^\circ \pm 0.6^\circ$, $71.4^\circ \pm 2.1^\circ$ and $67.0^\circ \pm 1.5^\circ$, respectively. Using AFM image of calix[4]arene LB films the rms values are calculated between 2.38 nm and 13.02 nm. It is thus concluded that the calix[4]arene films on the glass surface are uniform, dense, and homogeneous with some surface aggregates. SEM images also showed that the morphology of LB films were different than that of bare glass substrate. To investigate the kinetic response of calix[4]arene derivatives as an LB film to chloroform, benzene, toluene, and ethanol vapors, the resonance frequency is recorded as a function of time. The compound **2** yields the highest response to chloroform vapor with a fast and almost fully reversible response in a matter of a few seconds. When exposed to other vapors, compound **2** LB film is more selective to chloroform than other vapors with a large, fast, and reproducible response. This study concludes that *p*-*tert*-butyl group in the structure of calix[4]arene molecule can play a significant role for the organization of the LB film monolayer at the A/W interface, the deposition of LB films onto the solid substrates, and the detection of organic vapors for the sensor industry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.09.008>.

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Table 3
Response and recovery times of LB films of calix[4]arene molecules.

LB films	Response time (s)	Recovery time (s)
Compound 1	6	10
Compound 2	3	10
Compound 3	3	8
Compound 4	4	13

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