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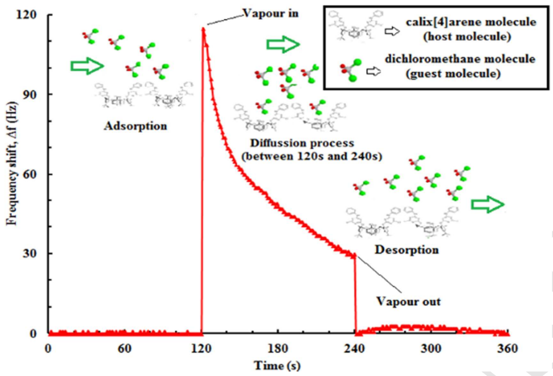
GRAPHICAL ABSTRACT



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ABSTRACT

A novel triazine-calix[4]arene conjugate was designed and synthesized with the aim to study gas sensing against volatile organic compounds (VOCs) such as dichloromethane, chloroform and carbon tetrachloride. This novel compound was fully characterized by spectroscopic techniques such as FTIR, ^{1}H and ^{13}C NMR along with HRMS and BET analysis. The triazine based calix[4]arene organic materials were fabricated onto quartz glasses and quartz crystal substrates to form a thin film chemical sensor element by using Langmuir-Blodgett (LB) technique. Quartz Crystal Microbalance, UV-Visible Spectroscopy, Atomic Force Microscopy and Scanning Electron Microscopy techniques were employed to characterize all these LB thin film layers. Fick's Equations were used for analyzing the swelling process of LB thin film sensor and diffusion coefficient values of organic vapours for swelling were obtained. The initial experiments have revealed that new triazine appended calix[4]arene derivative exhibited an effective chemical gas sensor characteristic with a large response to dichloromethane vapour.

Keywords: Calix[4]arene, Triazine, Chemical sensors, Volatile organic compounds, Quartz crystal microbalance.

1. Introduction

In recent years, supramolecular network designing and synthesis has served a very important purpose as it has been involved in various chemical and biological processes such as pollution of environment, enzyme-substrate binding, cell migration and organic solute transport [1]. In this sense, especially for the removal of harmful pollutants from the environment, the effective design and synthesis of novel macrocyclic systems with the ability of selective molecular recognition has become an important goal in supramolecular host-guest chemistry [2–4]. Non-covalent interactions (NCI) occupying a prominent place in host-guest chemistry such as hydrogen bonding, multipole-multipole interactions, π-stacking, cation-π and anion-π interactions are well-established essentials of chemical sensing in the construction and description of these supramolecular architectures [5].

In this field, calix[n]arenes representing a versatile and powerful class of macrocycle family have been extensively in use in the formation of supramolecular structures thanks to their availability, bowl shaped unique constitution and easy functionalization at lower and upper rims [6–8]. Among all kinds of calixarenes, calix[4]arene have been the most extensively studied one as host molecules because of being the most easily modified and arrangeable skeleton with the various reactions such as sulphonation, nitration, etherification, esterification, formylation and also showing the best complexation properties owing to its macrocyclic cavity and electronic features of substitutions [3, 9–12]. Thus, of course, besides their primary use as a sensor in gas adsorption, ionic and molecular recognition, calix[4]arenes have found numerous applications in diverse areas such as drug carriers, transmembrane transport, fabrication of metal-organic frameworks, liquid crystals, stationary phases and organic catalysts [13–22].

On the other hand, 1,3,5-triazine, also known as *s*-triazine, is another remarkable molecule for supramolecular chemistry with six membered ring containing three nitrogens owing to its high tendency to give reactions particularly substitution (S_N^2) reactions [23, 24]. Many attractive structures can be given as an example consisting of acceptor *s*-triazine core containing 1,2,3-triazole, ferrocene, thiophene, bisphenylaminobenzene, tetrathiafulvalene, 2-pyridyl and styrylbenzene subunits as donors [25, 26]. In this sense, within the appropriate choice of donor subunits and use of melamine derivatized triazine main frame, this molecule has been a challenging subject for materials chemistry in terms of its use as functional materials (e.g. luminescent active compounds, gas sensors, phosphorescent OLEDs, absorption of surfactants and nanoporous membranes for desalination) [25].

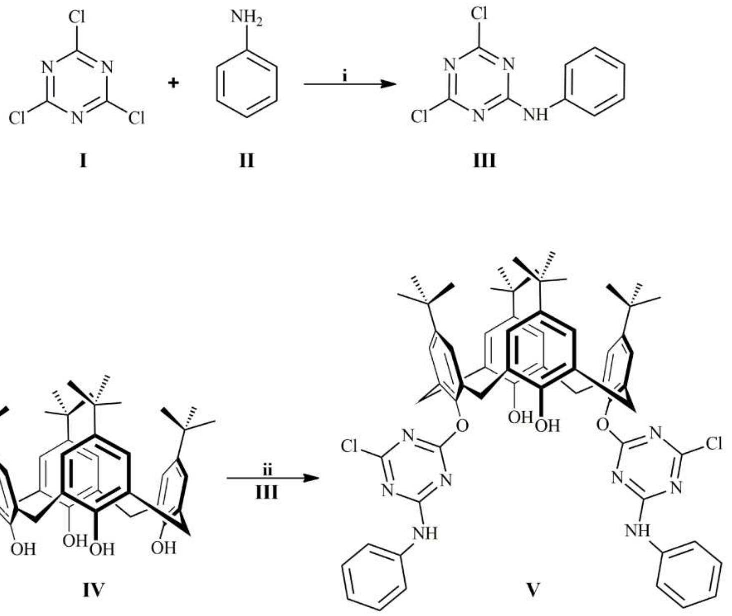
However, to the best of our knowledge and literature survey, calix[4]arene molecules along with *s*-triazine have been rarely studied on binding solvent molecules although they have exhibited excellent complexation abilities for small organic molecules together. So we have considered that triazine based calix[4]arene derivative can be effective for sensing organic vapours such as chloroform, dichloromethane and carbon tetrachloride.

From the perspective of such information, in this study, we would like to report the design and the synthesis of a new calix[4]arene derivative based on aniline bearing *s*-triazine conjugate system which was benefitted from its interactions (halogen-heteroatom, halogen-halogen, halogen-π) with solvent molecules used in the experiments. After synthesis and preparation of thin films utilizing LB thin film method, the related films were exposed to some saturated VOC vapours in order to investigate the swelling period in chemical sensor experiments [27]. These volatile organic compounds were easily detected by means of the appropriate cavity and host–guest inclusion interaction [28]. With the help of Quartz Crystal Microbalance (QCM) measurement system, variations in the resonance frequency were monitored concurrently with swelling when organic vapour was introduced into a gas cell [29]. The QCM results were fitted by using Early-time Fick’s law of diffusion equations. The results revealed that our calix[4]arene LB film material has been an excellent sensor for dichloromethane with high order sensitivity and selectivity, and deserve the chance for further applications in the development of hazardous organic vapour sensing devices.

2. Results and discussion

2.1. Design, synthesis and characterization of V

Mono-substituted triazine derivative **III** was prepared through the condensation of cyanuric chloride **I** and aniline **II** at 0°C under N_2 atmosphere (Scheme 1). For the synthesis of a triazine-calix[4]arene conjugate bearing two aniline units at the calixarene lower rim, calixarene derivative **IV** [30], blocked in a cone conformation by the introduction of *tert*-butyl groups at the upper rim, was selected as the starting main skeleton. Subsequently, another substitution reaction between **III** and **IV** in acetone at reflux gave the target compound **V** with 80% yield (Scheme 1).



Scheme 1. Synthesis of the target triazine-calix sensor candidate V. Reagents and conditions: (i) acetone, 0°C; (ii) K_2CO_3, acetone, III, reflux.

The target novel conjugate was characterized by IR, ^{1}H and ^{13}C NMR spectroscopy and HRMS analysis that provided compatible data for the expected molecular structure. Of course, in the pioneering studies conducted in the past, structural determination of calixarene derivatives had left a somewhat clouded picture behind because of the regiochemical preferences [31]. After that, thanks to many synthetic studies trying to clarify this, it was elucidated that a given system could be fixed in preferred conformations by using appropriate reagent and reaction conditions [32–34]. In this regard, the solvent and the base themselves have some direct influence on the formation of isomers in the synthesis of calixarene derivatives [35–38]. This can be explained by the ion-pair tightness. When considered from this point of view, due to the strong metal template effect of K^{+} keeping two OH groups in their original position through the K^{+}–phenoxide interaction, phenoxide anions having K^{+} as a counteraction is not reactive. Thus, the conformation is apparently immobilized in the di-*O*-substituted stage [35]. In other words, even in the presence of excess III, the reaction stops in the di-*O*-substitution stage and the solvent (acetone) along with the base (K_2CO_3) we used in our work lead to the formation of di-*O*-substituted isomer (distal-cone calix derivative). Moreover, as the most probative, observing the sufficient number of ^{1}H NMR signals described in detailed below and coupling constants (for bridging methylene groups, J =13.6 Hz) has proved the substitution pattern.

In the ^{1}H NMR spectrum of compound **V**, singlets were observed for both *tert*-butyl groups of calix ring at 1.32 and 1.06 ppm, while the methylene bridge protons of this cone appeared as a pair of doublets located at 3.93 ppm and 3.41 ppm. Besides, the presence of resonances relative to the remaining calix protons along with aromatic protons of aniline units between 6.86-7.20 ppm evidenced the formation of the desired triazine-calix[4]arene conjugate (see Supplementary data). In the ^{13}C NMR spectrum, methyl carbons of *tert*-butyl groups in calix ring were observed at 31.2 and 31.6 ppm, while triazine ring carbons appeared at 171.3, 164.8 and 150.2 ppm (see Supplementary data). Moreover, the target compound **V** was further characterized by the presence of etheric C–O–C stretching band at 1169 cm^{-1} in the FT-IR spectrum (see Supplementary data).

2.2. Isotherm Graph and Transfer Ratio

Fig. 1 indicates the surface arrangement of triazine based calixarene monolayer (π-A isotherm graph) at the air-water interface at a value of pH 6. This graph was used to analyze the surface behavior and to calculate the area per molecule, a_m, for a floating monolayer at the air-water interface given by [39]:

$$a_m = \frac{AM_w}{cN_AV} \tag{1}$$

where A is the limited area of the molecules compressed by the moveable barriers (taken from Fig. 1), M_w (1058.14 g mol^{-1}) is the molecular weight of the triazine based calixarene, c (0.54 mg mL^{-1}) is the solution concentration, V (400 µL) is the solution volume spread over the air-water interface and N_A ($6.023x10^{23}$) is the Avogadro’s number. Using Fig. 1 and a method of extrapolating the linear region of isotherm to zero pressure, a_m was estimated to be 1.06 nm^2.

A suitable surface pressure from Fig. 1 for the triazine based calixarene LB film deposition process was found to be 22 mN m^{-1}.

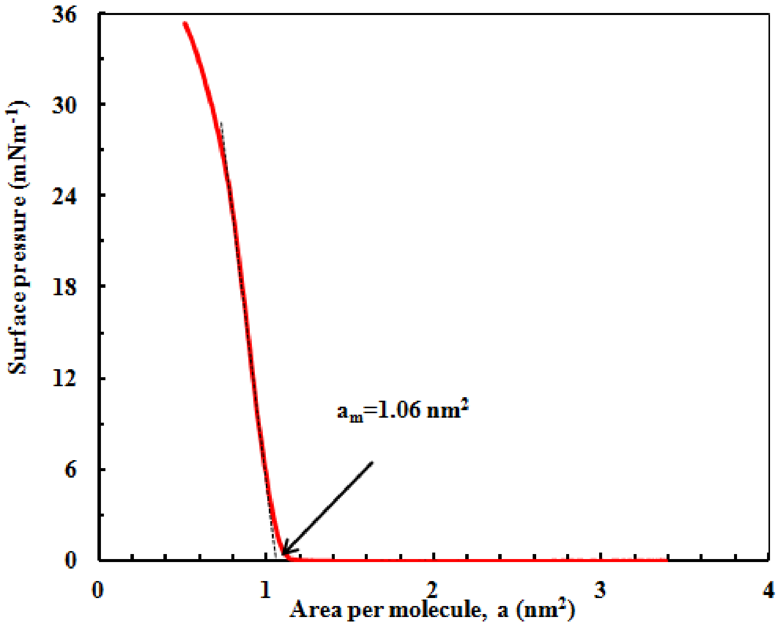


Fig. 1. Isotherm graph of the triazine based calixarene monolayer.

The deposition process of each LB film monolayer can be monitored to calculate the transfer ratio value (TR) given by:

$$TR = A_1 / A_2 \qquad (2)$$

where A_1 is given by reduced area of the monolayer on the water surface during the deposition process and A_2 is the area of coated LB film on the solid substrate. Decreasing of the monolayer area on the water surface for each bilayer should be equal to the transfer process of monolayer onto the solid substrate. Using Equation 2 TR ratio is calculated to be 96% for the triazine based calixarene and this result confirms that a uniform and reproducible LB film deposition was occurred during the LB film fabrication. It is also consistent with previous studies where TR value was calculated over 94% for the calixarene LB thin films [28, 40]. As a result, monolayers at air-water interface based on calixarene are suitable coating materials for LB films and can easily transfer onto quartz glasses and quartz crystal with a high transfer ratio.

2.3. SEM, AFM and BET results

Scanning Electron Microscopy (SEM) observations were made in a FEI Quanta 650 Field Emission model scanning electron microscope operated at 5 kV. SEM images were used for a comparison of SEM image of the bare quartz glass substrate (Fig. 2a) with the triazine based calixarene LB film (Fig. 2b) suggesting that a matrix of the triazine based calixarene molecules have been formed.

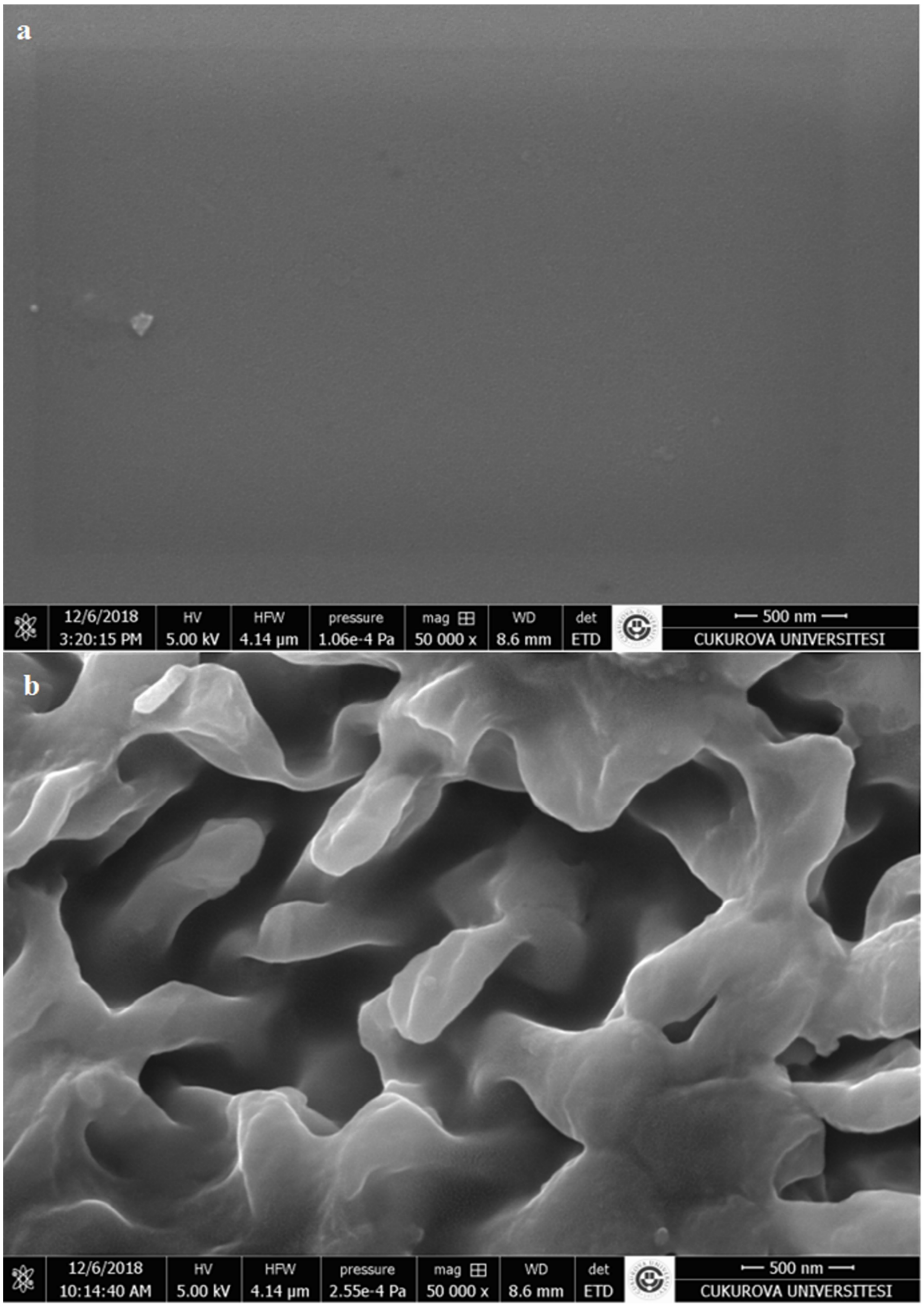
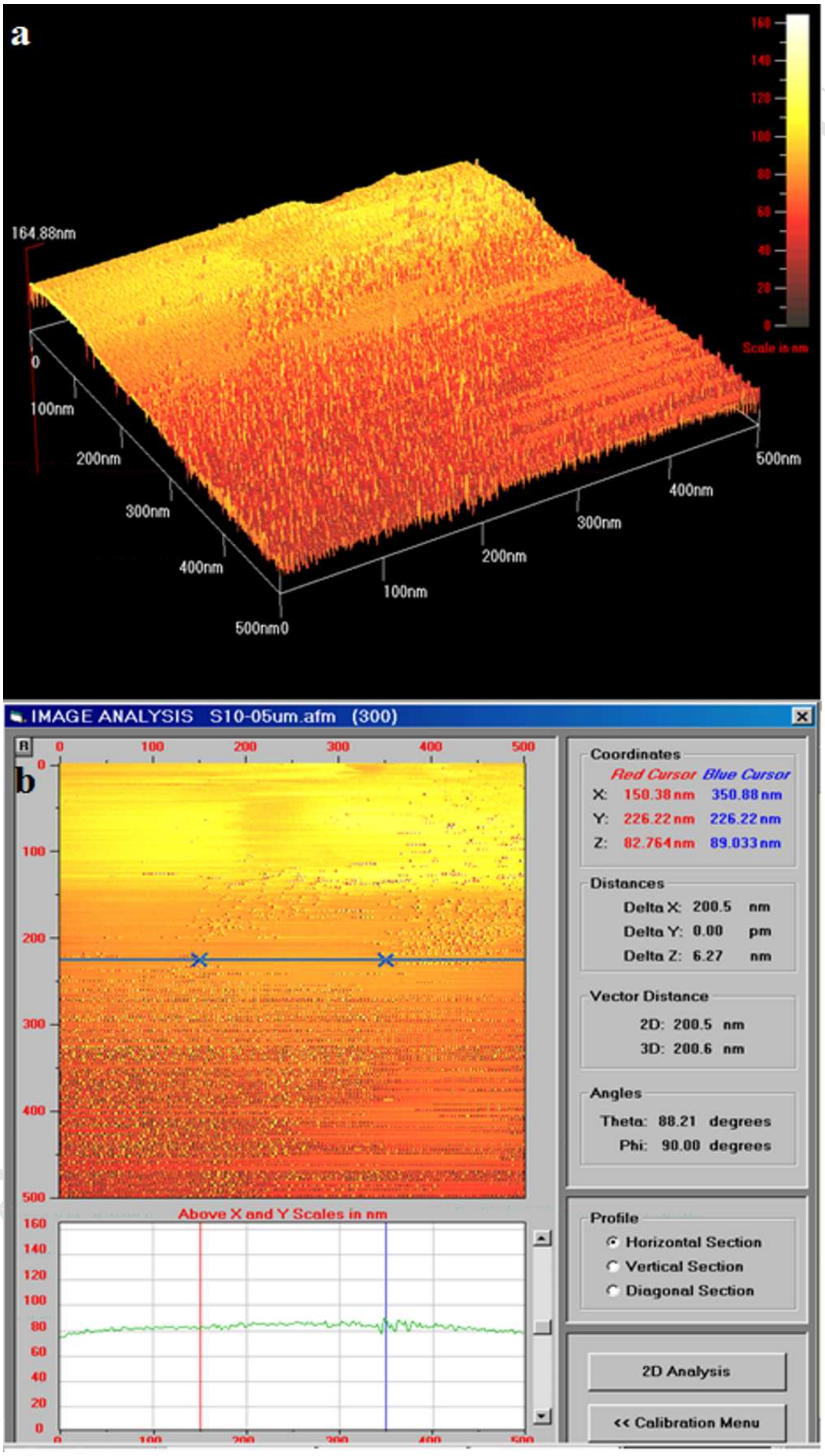


Fig. 2. SEM images of (a) the bare quartz glass substrate, (b) triazine based calixarene coated quartz glass substrate.

The surface investigations were conducted by using a Quesant-350 Atomic Force Microscope (AFM). The microscope was worked in contact mode and the typical force constant of the cantilever was used as 0.15 Nm^{-1}. The scan rate was applied as 1 Hz to investigate the thin film surface morphology. The 3D and 2D AFM images of LB film of the triazine based calixarene surfaces are presented in Figs. 3a–b, respectively. 2D AFM image (500 nmx500 nm) and the cross section of an calixarene thin film image were obtained by selecting the horizontal section as profile. Fig. 3b indicates the values of Z-axis (Red cursor: 82.764 nm and Blue cursor: 89.033 nm) on X and Y scale in nm. It can be said that the triazine based calixarene LB films on bare glass surface are uniform, close-packed, and homogeneous. AFM image shows that the triazine based calixarene LB film has a grainy form. This may be an advantage for gas sensing applications due to its high surface to volume ratio [41].



Coordinates

	Red Cursor	Blue Cursor
X:	150.38 nm	350.88 nm
Y:	226.22 nm	226.22 nm
Z:	82.764 nm	89.033 nm

Distances
Delta X: 200.5 nm
Delta Y: 0.00 pm
Delta Z: 6.27 nm

Vector Distance
2D: 200.5 nm
3D: 200.6 nm

Angles
Theta: 88.21 degrees
Phi: 90.00 degrees

Profile
● Horizontal Section
○ Vertical Section
○ Diagonal Section

Fig. 3. a) 3D AFM image of the triazine based calixarene coated glass b) 2D AFM image (500x500 nm^2) and the cross section of the triazine based calixarene coated glass.

The raw data provided by the BET analyzer instrument is in the form of a table indicating the volume of gas (nitrogen) introduced per mass of sample (cc/g), along with the relative pressure ($^{p}/_{p_0}$) during analysis. Also, the values of the adsorbed monolayer volume (V_m) and the specific surface area (*S)* can be calculated by using Equation 4 and Equation 5. Table 1 shows some data for the triazine based calixarene sample.

Table 1. Pressure and volume data from BET analysis of the triazine based calixarene.

Organic material	Relative pressure (p/p_0)	Volume Adsorbed V_a (cc/g)	$\frac{1}{V_a(^{p_0}/_{p} - 1)}$	Volume Adsorbed Monolayer V_m (cc/g)	BET Surface Area (S) (m^2/g)
The triazine based calixarene V	0.0453	1.611	0.0294	2.0651	326.5984
	0.0903	1.914	0.0518	2.0269	320.5612
	0.1361	2.152	0.0731	2.0515	324.4382
	0.1821	2.366	0.0941	2.0763	328.3669
	0.2288	2.508	0.1183	2.0339	322.6164

The generalized BET equation for gas adsorption can be described as follows [42]:

$$V_a = \frac{V_m C\, p}{(p_0 - p)[1 + (C-1)\left(\frac{p}{p_0}\right)]} \tag{3}$$

Here V_a is the adsorbed volume of gas, V_m is the adsorbed monolayer volume, p is the equilibrium gas pressure, p_0 is the saturation pressure and *C* is the BET constant (61.47). This equation can be rearranged as a linear function of $^{p}/_{p_0}$ as follows:

$$Vm = \frac{V_a\left(\frac{p_0}{p} - 1\right)[\left(\frac{p}{p_0}(C-1) + 1\right)]}{C} \tag{4}$$

The specific surface area (*S*, surface area per unit mass) can be found by the equation:

$$S = \frac{V_m\, N\, A}{22400\, m} \tag{5}$$

The constant *N* is Avogadro's number, *A* is the cross-sectional surface area of a single adsorbed gas molecule (0.162 nm^2 for nitrogen), *m* is the mass of nanomaterials used in the measurement (0.2753 g) and 22400 represents the Standard Temperature and Pressure (STP) volume of one mole of gas. This surface area (S) is given in units of area/mass (m^2/g).

Fig. 4 and the inset in Fig. 4 show plotted data from Table 1. The data in Table 1 can be used to calculate the specific surface area of the triazine based calixarene measured according to Equations 4 and 5. For the data shown in Table 1 and Fig. 4, the triazine based calixarene exhibits a BET surface area (the specific surface area) of about 324.51 ± 3.09 m^2/g. In the literature, similar analyses were carried out by Alahmadi et al. for the systematic and comparative study of the MCM-41 mesoporous silica functionalized *p*-sulfonatocalix[4]arene (C4S) and *p-tert*-butyl-calix[4]arene (PC4). In the relevant study, the BET surface areas of

MC4S and MPC4 were obtained as 452 m^2/g and 339 m^2/g, respectively [43]. In this context, it could be said that the BET value of our calix derivative V has been compatible for a porous structure.

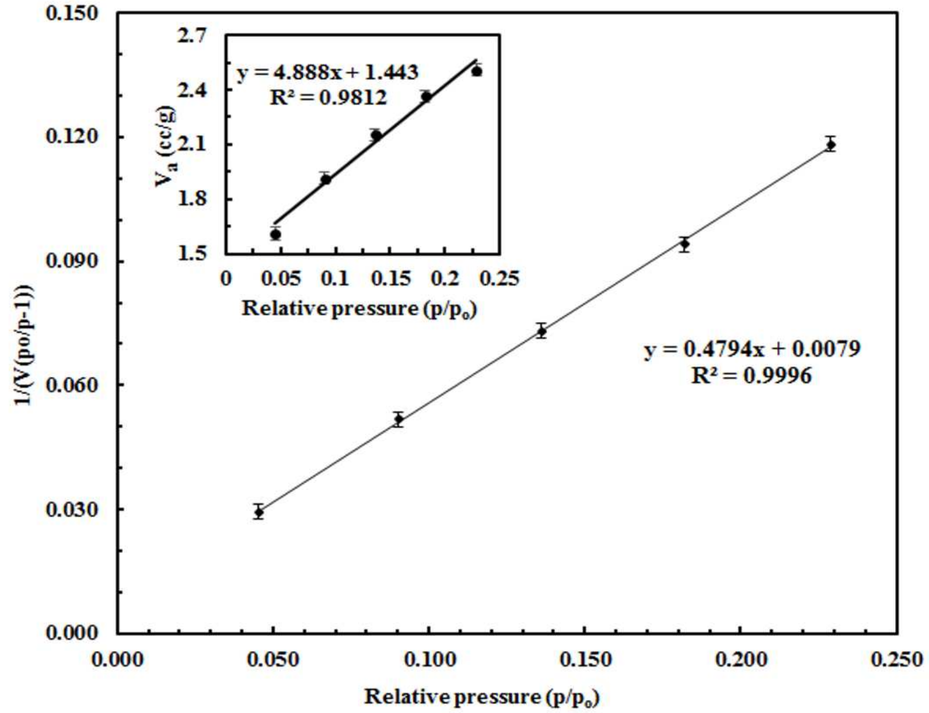


Fig. 4. BET plot of the triazine based calixarene. Inset: The adsorbed volume of nitrogen plotted as a function of relative pressure as measured during BET surface analysis of the triazine based calixarene.

2.4. UV-Visible results

Fig. 5 shows the UV-Vis absorption spectrum of calix[4]arene solution in chloroform along with UV-Vis absorption spectrum of various layers of calix[4]arene LB films fabricated onto a quartz glass substrate. The one of calix[4]arene LB film spectra exhibited an absorption band at 250 nm which coherence with the spectrum of chloroform solution (at 250 nm). Similar result was obtained for the UV-Vis spectra of 5,27-(Dipropylmorpholinoacetamido)-26,28-dihydroxycalix[4]arene LB films exhibited at 253 nm [28]. The inset in Fig. 5 also shows a plot of the absorption intensity at 250 nm relative to the number of layers of LB films and reveals almost a linear increase in the absorption intensity with the number layers. The linear relationship between absorbance and number of layers suggests that a regular deposition of the triazine based calixarene monolayer takes place, resulting in fairly uniform LB films. This means that similar amount of the triazine based calixarene is transferred during each LB deposition.

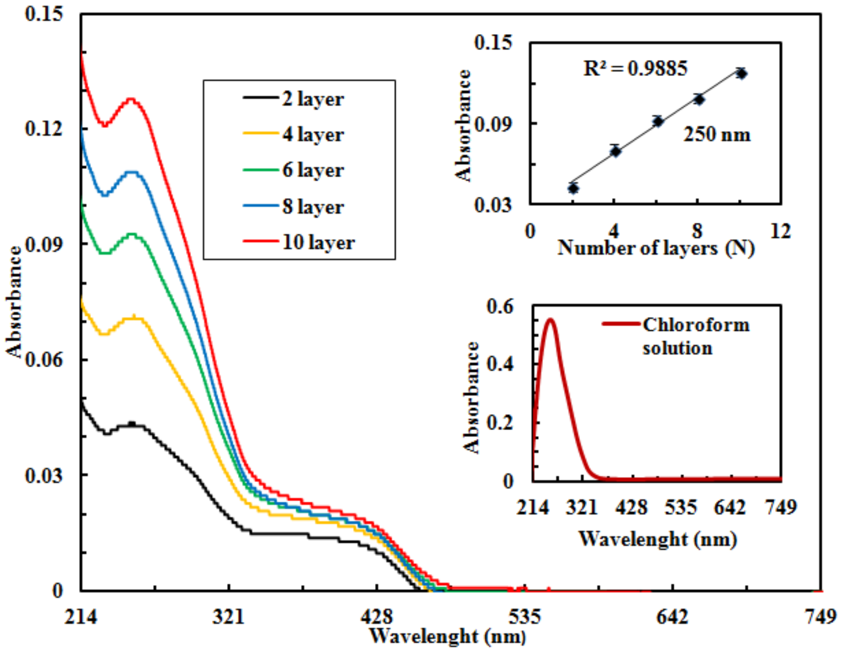


Fig. 5. UV-Vis spectra of the triazine based calixarene in a chloroform solution and the triazine based calixarene LB film on the quartz glass substrate. Inset: linear increase of absorbance as a function of layer numbers.

2.5. QCM results

QCM measurement technique allows us to study the mass change of quartz crystal surface deposited LB thin film as a function of resonance frequency. In here, a mass change per unit area (Δm) versus the resonance frequency change (Δf) on the triazine based calixarene LB film layer/multilayer quartz crystal is calculated from the Sauerbrey equation [44]. Fig. 6 shows the deposition of triazine based calixarene LB films onto a quartz crystal substrate for ten layers. It is clear that number of LB film layers is increased the resonance frequency shift is also increased. This linearity between Δf and N shows that a regular deposition of the triazine based calixarene onto the QCM substrate occurred adequately and equal mass of the triazine based calixarene is deposited per unit area. The frequency shifts of 44.91 Hz/per layer for the triazine based calixarene LB films are determined from the slope of Fig. 5. The amount of deposited mass on the quartz crystal substrate per bilayer is estimated as 692.76 ng (2.61 ng mm^{-2}) for the triazine based calixarene LB film using Fig. 6 and the Sauerbrey equation.

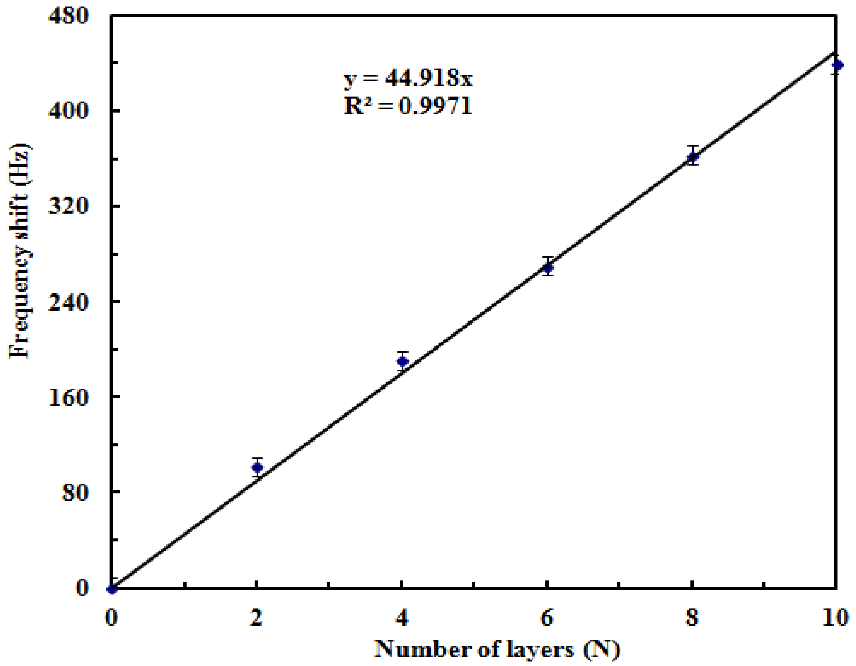


Fig. 6. The frequency shifts of the triazine based calixarene LB film against the number of layers.

2.6. Gas sensing properties of the triazine based calixarene

To investigate the chemical sensor properties of the triazine based calixarene LB film for hazardous organic vapour, the kinetic response of calixarene thin film sensor to dichloromethane, chloroform and carbon tetrachloride vapours is recorded by measuring the frequency changes as a function of time. The triazine based calixarene LB film is periodically exposed to the organic vapours for 2 minutes, followed by injection of dry air for a further 2 minutes period. Fig. 7 shows the kinetic response of triazine based calixarene LB film to the saturated vapours.

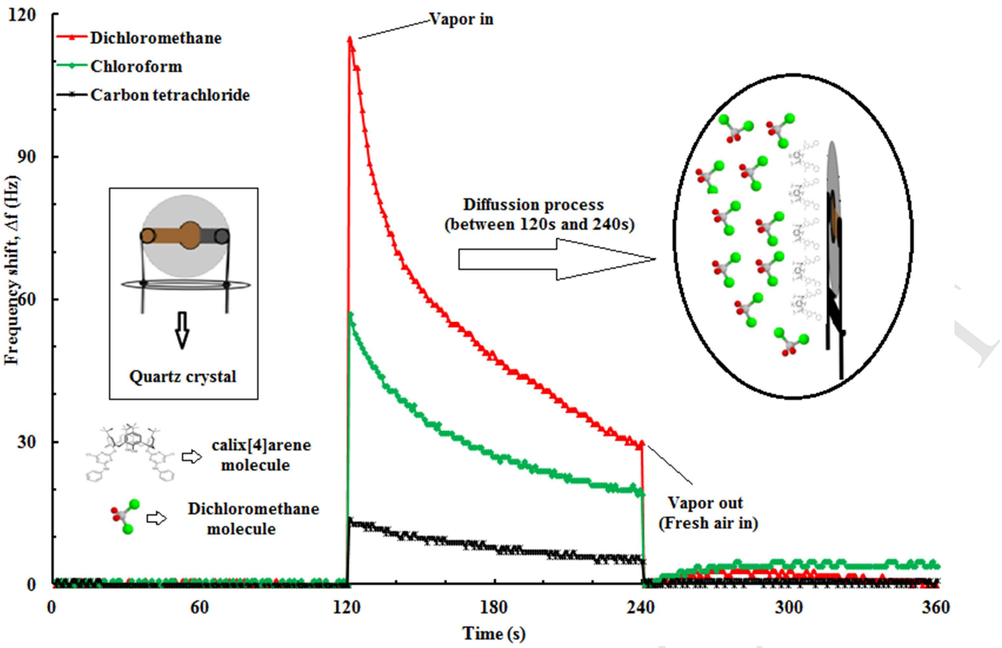


Fig. 7. The frequency change of the triazine based calixarene LB thin film against various chlorinated aliphatic hydrocarbons.

The QCM kinetic study was carried out by injection of dry air and organic vapour for 2 minutes, periodically. To ensure the response stability of triazine based calixarene LB film sensor, at the beginning film was exposed to dry air for 120 seconds and there was certainly no change at all seen in Fig. 7. When the triazine based calixarene film was exposed to saturated organic vapours, surface adsorption effect took place and a sudden increase can be seen. After the vapour molecules start diffusing into the triazine based calixarene film, frequency begins to change downward exponentially. For the recovery of film, dry air was introduced into the cell at the time of 240 s. Desorption of vapour molecules start between 240 and 244 s, and frequency values instantaneously return to initial values. These surface adsorption, diffusion and desorption processes refer to reproducibility, reversibility and sensitivity of the triazine based calixarene LB thin films. The triazine based calixarene LB thin film sensor is remarkably more selective and sensitive to dichloromethane vapour than other organic vapours. QCM kinetic measurements were repeated three times to ensure reproducibility of the sensor response. Table S1 shows the frequency change (Δf), response and recovery times of the triazine based calixarene LB film against organic vapours mentioned above. Calculations have been made for each organic vapour and are shown in Table S1. Also, the reproducibility of triazine based calixarene LB thin film sensor for dichloromethane vapour with different concentration values is shown in Fig. S1. When the concentration of vapour percentage increases, the frequency shifts increases proportionately.

The limit of detection (LOD) of the calixarene LB film sensor was calculated by the measured sensor sensitivity (Hz / ppm). LOD was defined by [28]:

$$LOD=3\sigma/S \qquad (6)$$

where, σ is the noise level of the fabricated QCM sensor, and S is the sensitivity to a specific analyte of the sensor. The sensitivity of LB film sensor was obtained from the frequency shift curve when exposed to dichloromethane in Fig. S4. The approximate value of the curve was obtained from this figure. In this study, the resonance frequency was recorded in air for use as the absolute frequency of the QCM system, and the frequency response was stable within ± 1 Hz over a period of 25-40 min. Therefore, the frequency noise was estimated at 1 Hz. The sensitivity of the calixarene QCM sensor to dichloromethane vapor was obtained as 5.99 Hz ppm^{-1}. Also, the detection limit performance of the calixarene QCM sensor to dichloromethane vapor was calculated as 0.50 ppm, at room temperature.

Besides, the experimental data of Fig. 7 were analysed (see Supplementary data) using the Early-time Fick's law of diffusion by following Fick's second equation which was reviewed by Crank [45]:

$$\left(\frac{\Delta f_t}{\Delta f_\infty}\right) = 4\sqrt{\frac{D}{\pi d^2}}\,t^{1/2} \tag{7}$$

where d is the thickness of the thin film, D is the diffusion coefficient, Δf_t and Δf_∞ are the normalized frequency shift at any time, t and saturation point in Δf , respectively. Fig. S2 displays the normalized frequency shift against swelling time. The normalized Δf values [$\Delta f_t / \Delta f_\infty$] are plotted in Fig. S3 for the square root of swelling time according to Equation 7. The slopes of the linear relations in Fig. S3 found the diffusion coefficients, D for the swelling of the triazine based calix[4]arene film.

As shown in Fig. 7, the resonance frequency change (Δf) of triazine based calix[4]arene thin film sensor for the organic vapours are observed as dichloromethane > chloroform > carbon tetrachloride. The values of resonance frequency change are found to be 115 Hz, 57 Hz and 14 Hz for dichloromethane, chloroform and carbon tetrachloride, respectively. Also, the values of diffusion coefficient are found to be 12.51x10^{-15} cm^{2}s^{-1}, 6.61x10^{-15} cm^{2}s^{-1} and 1.53x10^{-15} cm^{2}s^{-1} for dichloromethane, chloroform and carbon tetrachloride, respectively. Similar studies were carried out for the kinetic vapour sensing measurements of calix[4]resorcinarene LB films using ellipsometry, QCM, and SPR techniques. The results were explained by capillary condensation of VOC vapours in the nanoporous matrix of the calixarene LB films which result from swelling of the LB films due to surface adsorption effect [46]. The calix[4]resorcinarene thin film was exposed to several organic vapours and displayed a fast and reversible response. These results were also explained that the host-guest interaction between the cavity molecules and the organic vapour molecules [47, 48]. Also, the kinetic responses of LB films of calix[4]arenes containing *p*-*tert*-butyl groups and without *p*-*tert*-butyl groups for chloroform, benzene, toluene, and ethanol vapours were investigated as a function of time by using QCM technique. The results showed that after attaching *tert*-butyl groups onto the calix[4]arene structure, the response of LB film to chloroform vapour increased [13]. In addition to other gases, similarly, in our present work we investigated the sensitivity of our triazine based compounds against chloroform vapour by using QCM technique. We observed that the response of our LB thin film chemical sensor against dichloromethane was almost two times greater than for chloroform. This result could be explained with the substituted OH groups of calix[4]arene at 1,3-position by aniline bearing triazine units. Thanks to introducing of these units to the calix[4]arene skeleton, while the cavity has been expanding, the penetration of organic vapours has been greater.

The interaction between calix[4]arene LB thin film and relevant harmful organic vapours is considered to be a physical absorption via hydrogen bonding or dipole/dipole interaction [49]. The high values of resonance frequency change and diffusion coefficient obtained for dichloromethane vapour are compared with chloroform and carbon tetrachloride vapours. The inference which may be illuminated by the organic vapours′ high and low dipole moment values was previously presented in the literature [27, 50]. The order between dipole moment values and diffusion coefficient of organic vapours is similar (Table S1). This can be also explained with the fact that the molar volume of dichloromethane (64.10 cm^3 mol^{-1}) is lower than chloroform (80.70 cm^3 mol^{-1}) and carbon tetrachloride (97.10 cm^3 mol^{-1}). In this way, the penetration of chloroform and carbon tetrachloride molecules into the calix[4]arene LB thin films is slower and difficult while dichloromethane molecules can easily diffuse into the related films.

3. Conclusions

A new calix[4]arene derivative with triazine π-conjugate system has been engineered to perform chemical sensing. For this purpose, two mono-substituted triazine rings bearing aniline group have been tethered to the calix[4]arene scaffold. The target triazine-calix[4]arene conjugate has been obtained in good yield and the exact structure of this new compound was established by FT-IR, ^{1}H-, ^{13}C-NMR and HRMS analysis. The triazine based calix[4]arene LB film transferred onto the substrates with a reasonable high transfer ratio value of ~96%. A linear relationship between absorbance/resonance frequency and the triazine based calix[4]arene LB film layers indicates that the triazine based calix[4]arene molecule was orderly deposited as equal mass per unit area onto quartz glass and quartz crystal substrates for UV-Vis and QCM results, respectively. The frequency shift per layer and the deposited mass onto a quartz crystal were found to be 44.91 Hz per layer and 692.76 ng per layer (2.61 ng mm^{-2}), respectively. The triazine based calix[4]arene LB films were tested for their hazardous vapour sensing properties using QCM technique. According to the obtained results from sensing studies, it can be concluded that the triazine based calix[4]arene LB film sensor exhibited an effective chemical gas sensor characteristic with a large response to various chlorinated aliphatic hydrocarbons vapours (dichloromethane, chloroform and carbon tetrachloride). In conclusion, it was anticipated that good reorganization of units around calixarene skeleton along with H-bonding ability, π-π stacking and so host-guest interactions have played an important role in vapour sensing process.

4. Experimental

4.1. General

All commercially available (Merck and Sigma Aldrich) reagents and solvents were used as purchased. All experiments were performed under an atmosphere of dry nitrogen. While the reactions were monitored by thin layer chromatography (TLC) applied on silica gel 60 F_{254} pre-coated aluminum plates visualizing the spots under UV light at 254 and 366 nm, flash column chromatography was carried out using silica gel 60 (230 × 400 mesh) for purification of crude products. Melting points were measured on Gallenkamp electrothermal WA11373 melting point instrument in a sealed capillary glass tube without correction. FT-IR spectra were obtained on a Perkin–Elmer Spectrum Two spectrophotometer equipped with ATR sampling accessory. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian VNMRJ 400 spectrometer and reported in units of part per million (ppm) using tetramethylsilane (TMS) as internal standard (δ = 0 ppm). High resolution mass spectrum (HRMS) was recorded under electrospray ionization (ESI) conditions in positive ion mode using an Agilent 6230 TOF-MS instrument. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using a Costech Sorptometer KELVIN-1042 instrument. Sample was degassed at 100 °C during 2 hours in helium flow (carrier gas) before nitrogen adsorption.

4.2. Synthesis of the compounds III and V

4.2.1. 2-Phenylamino-4,6-dichloro-s-triazine (**III**)

Intermediate **III** was prepared in accordance with the method described in the literature [51]. To compound **I** (1.0 g, 5.42 mmol) dissolved in acetone (30 mL) at 0°C, aniline (1 eq) in 20 mL acetone was added dropwise and allowed stirring at 0°C for 2 hours along with TLC monitoring. After full conversion, the reaction was neutralized with 10 mL 10% Na_2CO_3 solution and then poured into the crashed ice. The precipated desired product was filtered, washed with cold water, and dried to obtain the title compound (1020 mg, 78% yield) as a white solid. M.p 197-198°C. FTIR (ATR) ν cm^{-1}: 3350 (NH), 1621 (C=N), 1608 (C=C), 1215 (C-N), 789 and 749 (C-Cl). ^{1}H NMR ($CDCl_3$) δ ppm: 7.67 (bs, 1H, NH), 7.51 (d, *J* =7.6 Hz, 2H, ArH), 7.39 (t, *J* = 7.6 Hz, 2H, ArH), 7.23-7.18 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ ppm: 171.34, 170.15, 164.03, 135.61, 129.29, 125.87, 121.33.

4.2.2. 25,27-(4-chloro-2-phenylamino-1,3,5-triazin)-26,28-dihydroxycalix[4]arene (**V**)

Firstly, a mixture of *p*-*tert*-butylcalix[4]arene **IV** [30] (570 mg, 0.88 mmol) and K_2CO_3 (2.4 eq) was stirred in 20 mL of acetone at room temperature for 24 hours. Then compound **III** (3 eq) in 20 mL of acetone was added and the reaction mixture was refluxed for 14 hours along with TLC monitoring. After the completion of the reaction, the solvent was evaporated under reduced pressure and flash column chromatography with silica gel was performed on the crude material using Hexane:EtOAc (10:1→6:1) to afford **V** (745 mg, 80% yield) as a white solid. M.p 309-311°C. FTIR (ATR) ν cm^{-1}: 3526, 2956, 2927, 1603 (C=C), 1552, 1169 (C-O-C), 1121 (C-O), 752 (C-Cl). ^{1}H NMR ($CDCl_3$) δ ppm: 7.20 (m, 4H, ArH), 7.12 (m, 4H, ArH), 7.03 (m, 2H, ArH), 6.94 (m, 4H, ArH), 6.86 (m, 4H, ArH), 3.93 (d, *J* = 13.6 Hz, 4H, ArCH$_2$Ar), 3.41 (d, *J* =13.6 Hz, 4H, ArCH$_2$Ar), 1.32 (s, 18H, C(CH$_3$)$_3$), 1.06 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$) δ ppm: 171.3, 164.8, 150.2, 150.1, 148.6, 148.4, 142.3, 136.9, 131.9, 128.8, 127.3, 125.7, 125.4, 124.1, 119.5, 34.1, 33.9, 31.6, 31.2. HRMS (ESI-TOF) calcd for $C_{62}H_{67}Cl_2N_8O_4$ [M+H]$^+$ 1057.4862, found 1057.4875; for $C_{62}H_{66}Cl_2N_8O_4Na$ [M+Na]$^+$ 1079.4721, found 1079.4726; for $C_{62}H_{66}Cl_2N_8O_4K$ [M+K]$^+$ 1095.4421, found 1095.4459.

4.3. LB film preparation

The investigation of NIMA 622 LB trough (a fully computer-controlled device) of an area of 1200 cm^2 considered the transfer of triazine based calixarene monolayer from the air-water interface to on suitable substrates. Solutions of the triazine based calixarene in chloroform with a concentration of ~0.49 mg ml^{-1} were prepared to take π-A isotherm graph. A duration of 15 minutes was given for the solvent to evaporate before the isotherm graph was taken and the temperature control unit was used to control the temperature of water subphase. All experimental data were collected at room temperature. The isotherm graph’s results were performed again three times more and found to be reproducible. After examining the π-A isotherm graphs, the floating monolayer at the water surface (at the surface pressure of 22.5 mN m^{-1}) was found to be stable for a period of 15 minutes. The value of surface pressure was selected for the LB film which is deposited on quartz glass and on quartz crystal substrates for both UV-Visible and QCM measurements. The LB film’s deposition mode was of the Z-type, and the vertical dipping process was performed with a speed of 25 mm min^{-1} at the selected surface pressure for both the down and up strokes. After each up-stroke LB film samples were allowed to dry. Under the similar surface pressure, various numbers of monolayer were placed on these substrates.

4.4. QCM technique

For QCM studies, the triazine based calix[4]arene material was fabricated onto quartz crystal substrates. After each deposition period, the LB film sample was left drying and the change in mass was checked utilizing the QCM measurement system controlled with a home-made computer. Dedicated software permits online recording of the variations in quartz resonance frequency. All the measurements were performed on an in-house designed oscillating circuit at room temperature with standard quartz crystals having a nominal resonance frequency of 3.5 MHz. The frequency of oscillation was checked as an element of time utilizing a PC after the quartz crystal was embedded into the electronic control unit. The frequency variation values which specify the amount of reaction, were measured with a precision of 1 Hz while providing organic vapour. Also, a gas cell was built to investigate the triazine based calixarene LB film reaction while exposing to organic vapours by measuring the frequency change. The calixarene thin film sensor was periodically exposed to organic vapours for 2 minutes and afterwards was allowed to recuperate after injection of dry air. And during exposure to organic vapours the variation in resonance frequency were recorded in real time. In order to observe the reproducibility of triazine based calix[4]arene thin film sensor this procedure was performed over several times.

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Scheme and Figure Captions:

Scheme 1. Synthesis of the target triazine-calix sensor candidate V. Reagents and conditions: (i) acetone, 0°C; (ii) K_2CO_3, acetone, III, reflux.

Figure 1. Isotherm graph of the triazine based calixarene monolayer.

Figure 2. SEM images of (a) the bare quartz glass substrate, (b) triazine based calixarene coated quartz glass substrate.

Figure 3. a) 3D AFM image of the triazine based calixarene coated glass b) 2D AFM image (500x500 nm^2) and the cross section of the triazine based calixarene coated glass.

Figure 4. BET plot of the triazine based calixarene. Inset: The adsorbed volume of nitrogen plotted as a function of relative pressure as measured during BET surface analysis of the triazine based calixarene.

Figure 5. UV-Vis spectra of the triazine based calixarene in a chloroform solution and the triazine based calixarene LB film on the quartz glass substrate. Inset: linear increase of absorbance as a function of layer numbers.

Figure 6. The frequency shifts of the triazine based calixarene LB film against the number of layers.

Figure 7. The frequency change of the triazine based calixarene LB thin film against various chlorinated aliphatic hydrocarbons.