



Optical parameters of calix[4]arene films and their response to volatile organic vapors

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ABSTRACT

The Langmuir–Blodgett (LB) technique was employed to produce thin LB films using an amphiphilic calix-4-resorcinarene onto different substrates such as quartz, gold coated glass and quartz crystals. The characteristics of the calix LB films are assessed by UV–visible, quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) measurements. UV–vis and QCM measurements indicated that this material deposited very well onto the solid substrates with a transfer ratio of >0.95. Using SPR data, the thickness and refractive index of this LB film are determined to be 1.14 nm/deposited layer and 1.6 respectively. The sensing application of calixarene LB films towards volatile organic vapors such as chloroform, benzene, toluene and ethanol vapors is studied by the SPR technique. The response of this LB film to saturated chloroform vapor is much larger than for the other vapors. The response is fast and fully recoverable. It can be proposed that this sensing material deposited onto gold coated glass substrates has a good sensitivity and selectivity for chloroform vapor. This material may also find potential applications in the development of room temperature organic vapor sensing devices.

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1. Introduction

Calix[*n*]arene materials have been extensively studied for several potential applications because of their synthetic flexibility and suitability for host–guest interaction. In the host–guest interaction, the conformational properties of these molecules allow the utilization of calix[*n*]arenes as fundamental building blocks that can be tailored to make calix[*n*]arenes with desired functionalities for quantitative and qualitative applications [1]. Most potential applications require that these materials should be prepared as a thin film form using a suitable technique [2]. Calixarenes and the related calix[4]resorcinarene derivatives in the form of thin films are of particular interest within the sensing community due to their selective recognition of different molecules. Films of controlled thickness of suitable calix[4]resorcinarenes can be easily fabricated using the Langmuir–Blodgett (LB) technique [3] onto varying substrate which were then used as chemical sensors. The cavity of the calix[4]resorcinarene provides a site for the binding of organic guest molecular species and the selectivity of calixarenes and calix[4]resorcinarenes to particular analytes can be controlled somehow by altering the size of the cavity as

well as the peripheral substituted groups. Most commonly, for calixarenes the cavity size corresponds to $n=4, 6$ or 8 and calixresorcinarenes are normally cyclic tetramers. A wide range of analyte species has been previously studied including metal ions and amino acids. Various analytical techniques have been used to follow the sensing response including UV–vis, surface plasmon resonance and quartz crystal resonance [4–7]. Various organic polymers and co-polymers, as well as special architecture low molecular mass molecules such as calixarenes, crown-ethers and phthalocyanines are commonly used as sensitive layer materials in gas sensors [8]. Langmuir–Blodgett (LB) films of resorcinarene molecules absorb water on their surface while more lipophilic solvents such as benzene and toluene penetrate into the volume of such films. Chemical gas sensor elements, which are based on discontinuous gold films coated with LB film of resorcinarenes, were shown to possess good sensitivity towards alcohols [9–11].

In the present work, a suitable calix[4]resorcinarene material is chosen to produce a thin LB film and to investigate the quality of LB film during the deposition process using UV, QCM and SPR. The thickness value and refractive index of this film are determined and sensing properties of this film against chloroform, benzene, toluene and ethanol vapors are studied. Our results showed that the sensitivity for the SPR signal to the exposure of chloroform vapour is quite high, stable and reversible.

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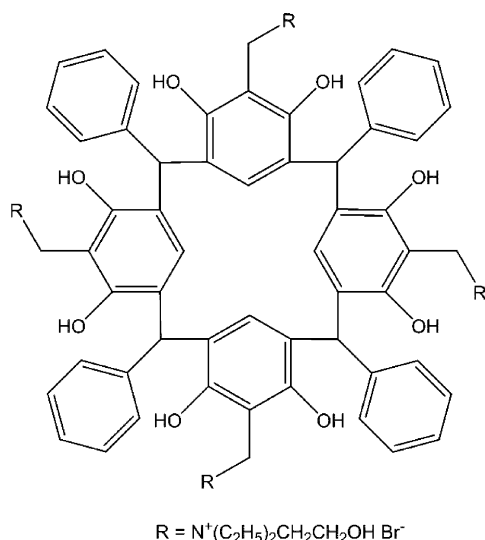


Fig. 1. The chemical formula of the CBTEA molecule.

2. Film preparation and experimental details

Fig. 1 shows the chemical structure of the material (CBTEA) which is initially synthesised as a resorcinol/benzaldehyde tetramer and then functionalised at the 2-position by a Mannich reaction with formaldehyde and diethylamine and then quaternised with 2-bromo ethanol to give an orange-coloured powder. The synthesis of this molecule and characterisation of its monolayers on various substrates has already been reported in the literature [2]. The amphiphilic character of the molecules containing hydrophobic aromatic side chains, and hydrophilic OH together with cationic ammonium groups makes them suitable for the LB deposition. A “NIMA 622 alternate layer LB trough” with an area of 1200 cm² was employed for the investigation of the CBTEA molecule at the air–water interface and for the fabrication of LB thin films. The temperature of the water subphase was controlled using a “Lauda Ecoline RE 204” model temperature control unit and all experimental data were taken at room temperature. 200 μl solution of CBTEA in chloroform with a concentration of ~0.2 mg ml⁻¹ were spread onto an ultra pure water subphase. A time period of 20 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. To investigate the behaviour of monolayer at the air–water interface, π -A isotherm graphs were recorded using a barrier compression speed of 200 cm² min⁻¹. The floating monolayer at the air–water interface was found to be stable at a surface pressure of 22.5 mN m⁻¹; therefore, this surface pressure value was selected for LB film deposition procedure. The deposition mode was Y-type with a speed of 25 mm min⁻¹ for both the down and up strokes. Several substrates such as a quartz slide for UV–visible measurement, a 50 nm thick gold coated glass slide for SPR measurement and a quartz crystal for QCM measurement were used as substrates for various measurement methods.

UV measurements were recorded with an Ocean Optics UV light source (DH-2000-BAL Deuterium Tungsten light source) and a spectrometer (USB4000) in absorbance mode in the range between 250 and 450 nm. UV spectra for CBTEA solution were taken in a quartz cuvette. After the deposition of LB film multilayer onto a quartz substrate, UV spectra were recorded as a function of layer numbers.

For QCM measurements, CBTEA LB film 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

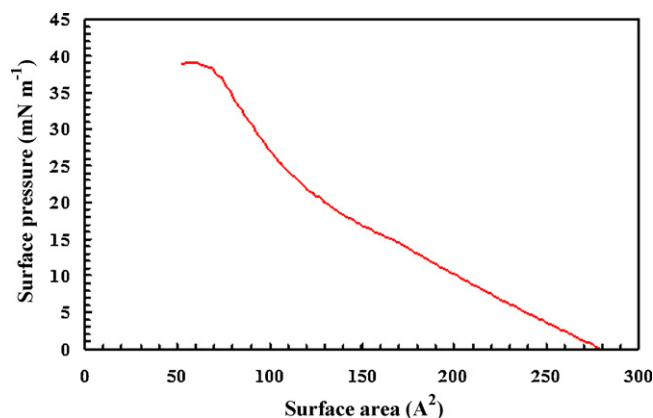


Fig. 2. Isotherm graph of the CBTEA monolayer.

was monitored using an in-house constructed computer controlled QCM measurement system with suitable software which allows the on-line recording of the changes of the quartz resonance frequency. The quartz crystal was inserted into the electronic control unit and the frequency of oscillation was monitored as a function of time. Values of frequency changes, which indicate the degree of response, are measured with an accuracy of 1 Hz when the organic vapor is present. All QCM measurements were taken at room temperature using a nominal resonance frequency of 9 MHz.

Surface plasmon resonance spectrometer (BIOSUPPLAR 6 Model) with a low power laser diode (630–670 nm) light source was employed to monitor the SPR spectra with an angular resolution about 0.003°. A glass prism ($n=1.62$) was mounted within a holder so as to be available for measurements in liquid or in air environments and glass slides with the dimensions 20 mm × 20 mm × 1 mm were coated on top by a very thin homogeneous layer of gold. A compatible transparent plastic flow cell with inlet and outlet connected to silicone tubes was used for organic vapor measurements. Several modes such as single measurements, tracking mode or slope mode could be utilized and the signal was displayed as a function of time. Biosuplar-Software was used to control the SPR system settings, measurements and data acquisition as well as data presentation. The photodetector response was recorded as a function of time during periodic exposure of the sample to the organic vapor for at least two minutes, which was then allowed to recover after injection of fresh air. WINSPELL 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. Results and discussion

3.1. Deposition properties

The pressure–area (π -A) behaviour or isotherm graph for a Langmuir monolayer is measured to understand how organic molecules can be arranged at the air–water interface and to assess the characteristic surface behaviour of an organic molecule on the water surface. Fig. 2 gives the pressure–area behaviour of CBTEA indicating the surface pressure as a function of enclosed surface area. As expected, the surface pressure increases when the surface area decreased and the monolayer begins to collapse at the surface pressure of about 38 mN m⁻¹. This graph was repeated several times and the results were found to be reproducible. Isotherms of calixarene materials with different substituted groups were extensively studied in the literature [5,6,12–14]. Our result shows a similar isotherm graph at the air–water interface. A stable LB monolayer is obtained at a pressure of 22.5 mN m⁻¹ and this value is

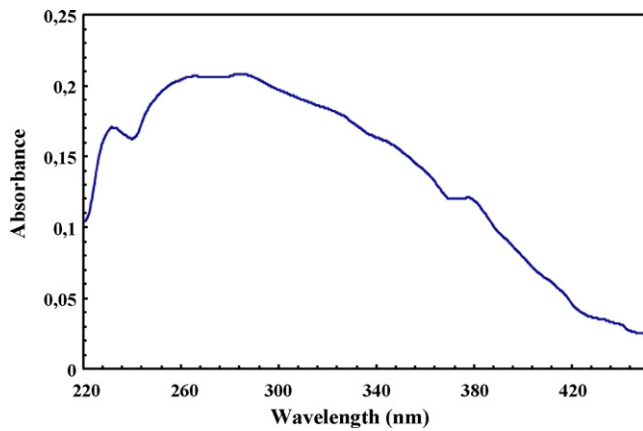


Fig. 3. The UV–visible spectra of a CBTEA solution.

selected for the LB film deposition. The deposition efficiency of the LB film 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. Its value is given as in Eq. (1):

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

where A_L is the decrease in the area occupied by the monolayer on the water surface and A_S is the coated area of the substrate. Using Eq. (1), a Y-type calix LB film is then obtained with a transfer ratio close to 0.95. This value can be used to conclude that steady, reproducible and uniform monolayers of CBTEA were deposited from the air–water interface onto a quartz crystal substrate.

3.2. UV–visible results

Fig. 3 shows the UV absorption spectra of a CBTEA solution in chloroform. A broad absorption band was observed at 280 nm. The UV characterisation of calix[4]arenes, carried out using different solvents, shows that the linear as well as the cyclic oligomers have a pair of absorption maxima near 280 and 288 nm [15,16]. When compared with our results, the same UV absorption spectral structures were observed at 285 nm for the CBTEA films [17–19]. A number of UV–vis spectra of CBTEA LB films transferred onto a quartz substrate with several different layer thicknesses are shown in Fig. 4. This shows that the absorption intensity increased when the number of layers increased. The UV spectra of the LB films are similar to the CBTEA spectrum of the solution form, except that

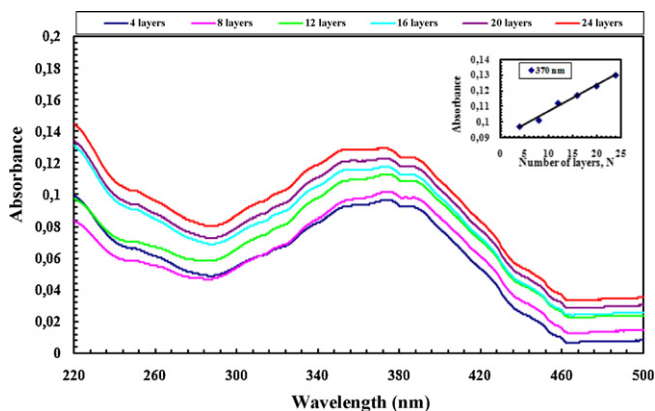


Fig. 4. UV–vis absorption of CBTEA LB films. Inset: linear relationship between absorbance and the number of bilayers, corresponding to the thickness of the films.

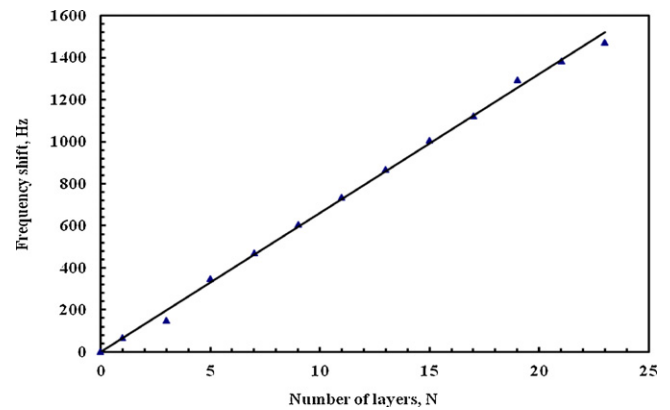


Fig. 5. Frequency changes as a function of layer numbers.

the bands at 280 nm is broadened in the solution spectrum and is red shifted by about 90 nm. This might be explained by the occurrence of molecular aggregation in the LB films. The shift in the absorption band of the LB film may be the result of some kind of molecular aggregation taking place during film formation, for which the wavelength increases while energy is reducing. A similar red shift is observed at the absorption maxima at 350 nm for calix[4]resorcinarenes LB film [2].

The inset in Fig. 4 shows variations of absorption intensity at 370 nm as a function of number of layers. This linear relationship confirms a fairly constant transfer ratio during sequential dipping of the slide through the LB monolayer. This demonstrates successful adhesion of the monolayers to the quartz substrate.

3.3. Quartz crystal microbalance (QCM) measurements

QCM sensors are based on the detection of the mass change in the sensing overlayer by the measurement of the resonance frequency of the device. The principle of measurement is the change by Δf in the fundamental oscillation frequency f_0 upon mass deposition on the quartz crystal surface. Thus, upon exposure, the analyte molecules are adsorbed by the sensing overlayer deposited onto the quartz crystal, causing a change in its mass and, in turn, a change in the fundamental oscillation frequency f , in accordance with the following frequency–mass relationship called Sauerbrey equation [20]:

$$\Delta f = - \frac{2f_0^2 \Delta m}{A \sqrt{\mu_q \rho_q}} \quad (2)$$

where A the surface area of electrodes (cm^2) of the quartz crystal, $\mu_q = 2.947 \times 10^{11} \text{ g/cm s}^2$ and $\rho_q = 2.648 \text{ g/cm}^3$ are the shear modulus and the density of the quartz substrate, respectively. Δm is the amount of mass change (g).

Fig. 5 gives the resonant frequency change of the quartz crystal as a function of the deposited LB film layers using a 9 MHz quartz crystal. QCM measurements were carried out at the room temperature. A linear relationship was observed between the frequency and mass change. This shows that an equal mass is deposited onto the quartz crystal and a uniform LB film is obtained using the CBTEA material. Using the gradient of Fig. 5 and Eq. (2), the typical frequency shift is estimated $\sim 66 \text{ Hz}$ per bilayer and the deposited mass per bilayer is calculated to be $0.92 \times 10^{-6} \text{ g}$.

3.4. Surface plasmon resonance (SPR) measurements

SPR curves indicating the dependence of reflected light intensity on the internal angle of incidence for the CBTEA LB films are shown in Fig. 6. These curves for the CBTEA layers are shifted with respect

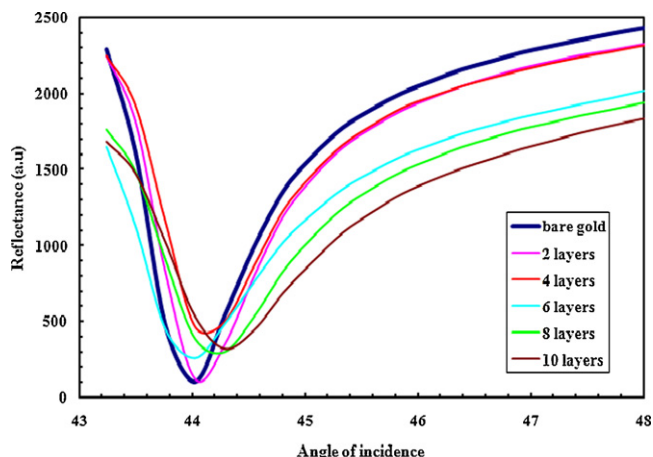


Fig. 6. SPR curves of CBTEA LB films with increase in thickness.

to the curve of a bare gold SPR curve in proportion with the number of LB layers.

The experimental SPR data were fitted using the Winspall software (written by Wolfgang Knoll, developed at the Max-Planck-Institute for Polymer Research, Germany) [21–24] in order to evaluate the film thickness (d) and its refractive index (n). It was assumed that $k=0$ for our LB films, since they are transparent at $\lambda = 633$ nm [6]. Fig. 7a and b presents the experimentally measured

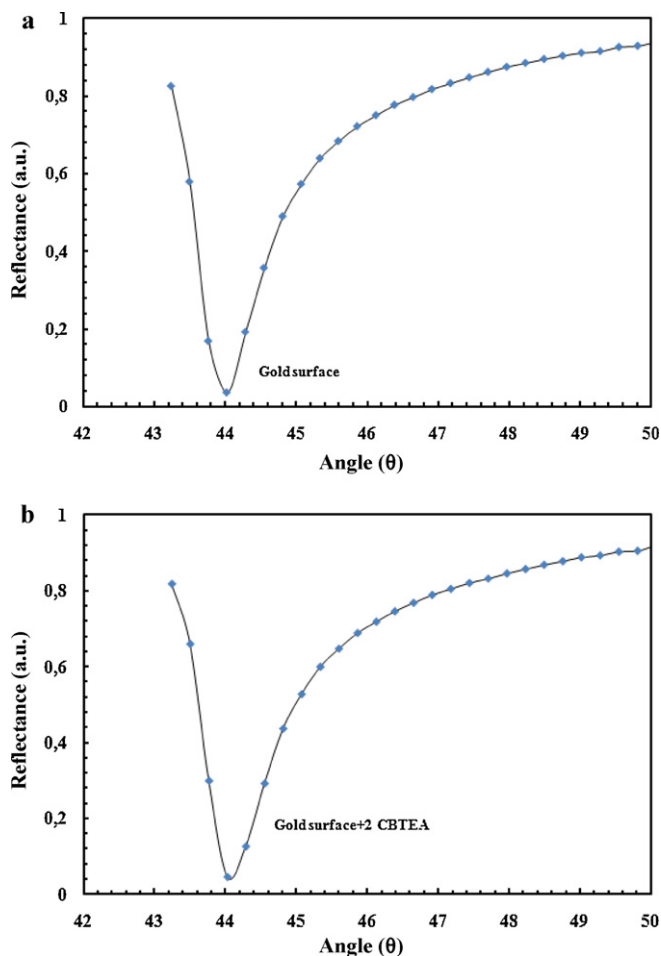


Fig. 7. (a) Complete measured (dots) and fitted (lines) SPR curves for clean gold surface, (b) complete measured (dots) and fitted (lines) SPR curves for 2 CBTEA LB film.

Table 1

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

Number of layers	Thickness (nm)	Refractive index
2	2.3	1.70
4	4.7	1.64
6	6.2	1.64
8	8.9	1.68
10	11.7	1.82

and theoretically fitted SPR curves for the uncoated gold film and for the same gold film coated with 2 monolayers of CBTEA. Similar calculations were carried out for 4, 6, 8 and 10 layers. Values of the thickness (d) and the refractive index (n) of CBTEA LB films obtained by the Winspall curve fitting program are given in Table 1. The fitting calculations produce a mean value of 1.14 nm for the thickness per monolayer, and values between 1.64 and 1.82 for the refractive index. For the refractive indices of calix[n]arene ($n = 4, 8$) thin films, similar results were obtained by [4,6,25], 1.46 by [26,27], 1.494 by [28], 1.48 by [29] and between 1.54 and 1.43 by [30] respectively. Katantseva et al. studied the refractive index and thickness of several calix[n]arene molecules and determined refractive indices between 1.47 and 1.70 along with thickness values from 0.80 to 1.50 [31].

4. Sensing properties

The SPR technique was used in order to investigate the adsorption properties of CBTEA LB films. Both steady state and in situ adsorption kinetic characteristics were obtained. This allowed a comparison of the sensitivity of the device to four volatile organic compounds (VOCs) and the determination of the selectivity of the sensor. Fig. 8 shows that adsorption of the volatile organic vapour causes an increase in the thickness and the refractive index of the LB film [4]. The mechanism of adsorption consists of incorporation and accumulation of the volatile organic vapour from the gas phase into the nanoporous calixarene matrix, which is accompanied by swelling of the film [23,26]. Adsorption and desorption processes are very fast and a full recovery of the LB film occurs. The sensitivity for the SPR signal to the exposure of chloroform vapour is quite high. Results obtained also show the possibilities for the development of optical sensors for aromatic compounds based on calix[4]arene LB films.

Sensitivity and selectivity of the film to chloroform, benzene, toluene and ethanol vapors were studied using SPR measurements.

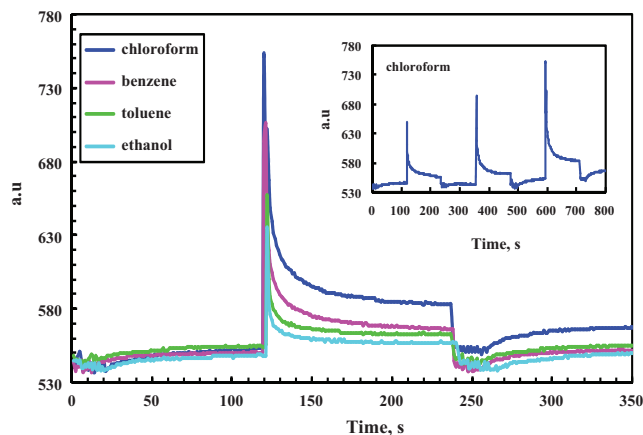


Fig. 8. Kinetic response of sensors coated with CBTEA (10 layers) to injection of volatile organic vapors into working cell. Inset: reproducibility of the film for chloroform.

The CBTEA sensing film was found to be stable and exhibited no significant losses in sensitivity when the measurements were repeated many times. Fig. 8 displays a set of typical curves showing the reflection intensity as a function of time when the CBTEA LB film is exposed to saturated volatile organic vapors for 2 min followed by clean air for a further 2 min period. The value of the photodetector response is proportional to the changes in reflectivity since the measurements were carried out within the linear part of the SPR curves. It can be seen that its response to all vapors are very fast and reversible. Such behaviour of sensors can be explained by the interaction between the chemical structure of material and the organic vapour. For example, increasing the calixarene cavity size leads to higher magnitudes of responses to injection of vapors of chlororganic compounds [25,32,33].

It can be concluded that the CBTEA LB film studied here shows some response to all vapors and is more sensitive towards chloroform than for other vapors. This might be due to the stronger polarity of the chloroform molecules, allowing them to form a stronger interaction with the sensing material; consequently more molecules are adsorbed. A similar response to chloroform was reported for the sensors based on different calixarene materials [32,34,35]. The lowest response was given to toluene having a benzene ring and to ethanol. It seems that the physico-chemical properties of gas molecules such as their polarity have an influence on the adsorption behaviour when the gas molecules are adsorbed by the sensing films. The different absorption behaviour of toluene and benzene observed in our studies may be attributed to the different symmetry and polarity of their molecules along with the lower saturated vapour pressure of toluene. In toluene this property is due to the CH₃ group in it.

5. Conclusions

In summary, we have studied the optical and gas sensing properties of calix[4]arenes derivatives. CBTEA was produced and deposited as LB films on quartz, gold-coated glass and quartz crystal substrates. The films were characterised optically by means of UV, QCM system and SPR. Isotherm graph results indicated that this molecule gives a stable monolayer at the air–water interface and a surface pressure value of 22.5 mN m⁻¹ at solid phase is selected for the LB film deposition. A plot of UV absorbance, measured at 370 nm as a function of number of layers gives a linear relationship. This proved that this material can be deposited onto a quartz substrate. Similar linear relationships were obtained with respect to the deposited mass onto quartz crystal substrates which was then utilised for QCM measurements to determine the resonant frequencies versus layer number [36,37]. A slope change occurred for small number of layers indicating a deposited mass value of 920 ng per monolayer. According to our SPR results, the LB film transfer onto gold-coated substrates was found to be successful and monolayers were transferred uniformly onto the gold-coated glass substrate. The film thickness t and refractive index n of CBTEA LB film was found to be $t = 1.14$ nm/deposited layer and $n = 1.6$, respectively. Monolayer thicknesses derived from SPR reflectance curve fitting were in good agreement with the above findings, and optical parameters obtained compare very well with those found in the literature [13].

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