Langmuir–Blodgett thin film for chloroform detection

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ARTICLE INFO

ABSTRACT

Calix[4]resorcinarene (C11TEA) molecules could be deposited as an LB film by the Langmuir–Blodgett (LB) technique onto suitable substrates. Surface plasmon resonance (SPR) and UV–vis spectroscopy were employed for the characterization of these LB films. A high quality and uniform Langmuir monolayer from the water surface can be transferred onto a glass or gold coated substrates with a transfer ratio of over 95%. Thickness and refractive index values of the resultant LB films were measured using surface plasmon resonance with a value of 1.04 nm per layer and 1.4 respectively. For the sensing application towards chloroform, this LB film yields a fast and almost fully reversible response to chloroform in few seconds.

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1. Introduction

The name calixarene was proposed by Gutsche for a series of cyclic oligomers, readily obtained by treatment of p-alkylphenol with formaldehyde and a suitable base. As well as these compounds, a similar class of materials, can be synthesized by the acid catalyzed condensation of a number of aldehyde to give cyclic tetramers, known as calixresorcinarenes [1]. Calix[n]arenes are known to be excellent Langmuir and Langmuir–Blodgett film forming materials and they are used as specific ligands for analytical chemistry, sensor techniques, and medical diagnostics, since a number of synthesis methods allow flexible variation of their ring size, they can be functionalized with a wide range of functional groups, and have structural characteristics such as high porosity and good chemical stability [2]. Chemical sensors based on relatively low cost synthesis calixarenes and calixresorcinarenes were designed to detect various inorganic gases [3], explosive vapours [4] and volatile organic compounds (VOC's) [5,6] because of their flexible structure, as well as their wide range of physical and chemical properties that can be tailored by changing their compositions.

The monitoring and detection of VOC's has become a serious aspect to consider because the need to control air quality has become an environmentally important issue. The construction of gas and VOC sensors will allow the rapid detection of harmful or environmentally damaging vapours without the need for techniques such as gas chromatography or mass spectrometry which often require expensive equipment and highly trained laboratory personnel. Improving the performance of gas sensing devices mostly depends on the sensitivity and selectivity of the sensing materials. It is well known that when a gas molecule is adsorbed onto the surface of an organic material, the physicochemical properties, including the structural, electrical, and optical properties, of this sensing material can change. This has led to intensive research into new materials with the ability to bind, detect and identify organic vapours. The chief difficulty in gas identification continues to be the fabrication of stable sensors with a high sensitivity and selectivity towards the substance to be detected. Because of the sensitivity of calixarenes to organic vapours and their excellent LB film forming ability, we have investigated in depth the use of these materials to sense VOCs. Previous work has demonstrated sensitivity of calixresorcinarene films to BTEX gases [5] and a range of common organic solvents [6,7]. A number of other authors have also carried out studies on these systems, for example SPR could be used to measure the adsorption of a range of organic compounds onto calixarene thin films [8]. Other workers deposited an amine-modified calixresorcinarenes as LB films onto piezoelectric quartz crystals and showed their sensitivity to a range of organic vapours, demonstrating that both
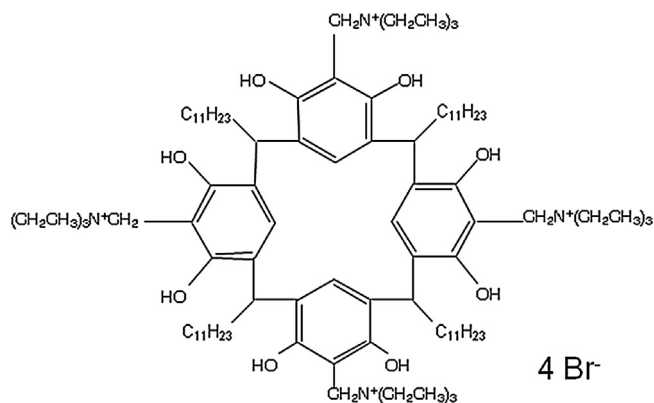
Fig. 1. Chemical structure of C11TEA.

the pH of the subphase and the presence of copper ions affected the sensitivity of the films [9]. In other work, calixarenes were deposited both as LB and cast films [10] and tested for their sensitivity towards aromatic hydrocarbons using piezoelectric mass sensors, cast films were shown to be more sensitive but LB films displayed greater selectivity. A novel calixarene–porphyrin compound could also be deposited as an LB film and shown to demonstrate changes in optical adsorption on exposure to amine vapours [11]. One of the materials studied was specific to secondary amines and displayed no sensitivity to primary and tertiary amines. Similar tetramers based on pyrrole rather than phenolic units have also been shown to form LB films and display sensitivity to alcohols when assessed using surface plasmon resonace [12,13].

Tetraundecyl resorcinarene was derivatised using a Mannich reaction with paraformaldehyde and diethylamine [14]. The resulting tetramine was then refluxed with five equivalents of ethyl bromide in ethanol for 16 h, volatiles removed and the calix recrystallised from ethanol. Calix[4]resorcinarene (C11TEA) was chosen as it forms good quality LB films and similar materials have also been shown to react to aqueous guests [15]. It was also hypothesized that the presence of cationic ammonium substituents would effect both the size and electron density of the cavity, potentially improving it's binding properties and enhancing sensitivity towards certain vapours. In this study, the preparation of LB film of the C11TEA given in Fig. 1 was evaluated at the water surface using isotherm graphs. Surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) systems were used to demonstrate the thin film deposition on a gold coated glass substrate and to determine the thickness and refractive index of LB film. Furthermore we utilized this LB film as the active component within a sensor for organic vapours such as chloroform, benzene, toluene and ethyl alcohol.

2. Experimental details

2.1. LB film preparation and deposition

A computer controlled NIMA 622 alternate LB trough was employed to study the molecular behaviour of C11TEA molecule at the air–water interface and to produce LB films onto glass and gold coated glass substrates. Before each experiment, the barriers and the Teflon trough of the LB film system were rinsed with ultrapure water (18.2 MΩ cm) after being cleaned with chloroform. The surface pressure was measured by using a Wilhelmy balance, equipped with a strip of chromatography paper suspended at the air–water interface at 20 °C which was controlled using Lauda Ecoline RE204 model temperature control unit. C11TEA molecule was dissolved in chloroform with a concentration of 0.2 mg mL^{-1} and

was 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. A time period of 20 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. The pressure–area (π–A) isotherm graph was determined with the accuracy of 0.1 mN m^{-1}. This graph was recorded as a function of surface area using the compression speed of barriers at a value of 172 mm^2 min^{-1}. A quartz slide for UV–vis measurement, a 50 nm gold coated glass slide for SPR measurement and a quartz crystal for QCM measurement were used as substrates for various measurement methods. 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 the LB film deposition procedure. 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.

2.2. SPR measurements

A surface plasmon resonance spectrometer (BIOSUPLAR 6 Model) with a low power laser diode (630–670 nm) light source was employed for the measurements with an angular resolution of about 0.003 degrees. A glass prism ($n = 1.62$) mounted to onto a holder is available for measurement in liquid or in air. The glass slides had the dimensions of 20 mm × 20 mm and the total thickness was 1 mm are coated on the top by a 50 nm thin gold layer. After each deposition cycle, the C11TEA LB film sample was dried for half an hour and the SPR curve was monitored using SPR measurement system. This system was used for the confirmation of the reproducibility of LB film multilayers using the relationship between the angle changes against the deposited thickness, which should depend on the number of layers in the LB film. WINSPALL software developed in the group of Max-Planck-Institute for Polymer Research (by Wolfgang Knoll), Germany was utilized for fitting of SPR curves are used to determine thickness and refractive index values of LB film.

Chloroform (99% Merck), benzene, toluene and ethanol (99% Aldrich) were used without further purification as organic vapours for the detection performances. All 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]resorcinarene LB films [7,8]. A special flow cell from transparent plastic, compatible for vapor or gas measurements was constructed to study the kinetic response of C11TEA LB film on exposure to organic vapours by measuring the reflected light intensity changes. The cell has two channels, with inlet and outlet connected to silicone tubes. The SPR system is completely controlled by the Biosuplar-Software which handles the settings, the measurements and data acquisition as well as controlling to measurement and data presentation. VOC injections were performed with a syringe. The concentration values of organic vapor (can be seen in Table 1) in ppm can be calculated by the formula as follows [16]:

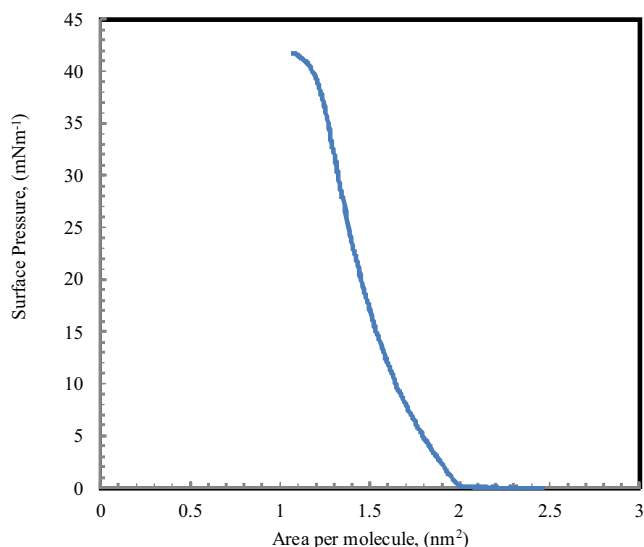$$c = \left[\frac{24.055 \rho V}{M V_0} \right] \times 10^6 \qquad (1)$$

Fig. 2. The isotherm graph of a C11TEA monolayer at the air–water interface.

where c (ppm) is the concentration of vapor, ρ (g/mL) is the density of vapor, V (mL) is the volume of vapor which is injected into the gas chamber, M (g/mol) is the vapor molecular weight, and V_0 is the volume of the gas chamber ($\sim$0.02 mL).

The response was recorded as a function of time when the sample was periodically exposed to the organic vapours for at least 2 min and was then allowed to recover after injection of dry air. This procedure was carried out during several cycles to study the concentration changes and to observe the reproducibility of the LB film sensing element.

3. Result and discussions

3.1. Deposition process

A pressure–area (π–A) graph for a Langmuir monolayer shows the characteristic surface behaviour of an organic molecule on the air–water interface. The area per molecule for an organic monolayer can be calculated using the following relation [17]:

$$a_m = \frac{AM_w}{cN_AV} \tag{2}$$

where A is the area of the water surface enclosed by the trough barriers, M_w the molecular weight, c the concentration of the spreading solution, N_A the Avogadro's number, and V is the volume of solution spread over the water surface.

Solutions (200 μl) were spread by a Hamilton microliter syringe onto the water surface by distributing the droplets over the entire trough area. A time period of 15 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. The π–A isotherm graph was obtained with the accuracy of 0.1 mN m^{-1}. Fig. 2 shows the isotherm graph of C11TEA. After the gas phase, C11TEA molecule shows a sharp increase until surface pressure of 40 mN m^{-1} and then monolayer at the air–water interface starts to collapse. A deposition pressure value of 22.5 mN m^{-1} was selected for monolayer transfer onto the solid substrates. Using Fig. 2, the limiting area per molecule obtained by extrapolating the slope of low compressibility to zero pressure in the condensed state and a value of 1.79 nm^2 for C11TEA was determined using Eq. (1). Similar results on the behaviour of area per molecule values of 1.71 nm^2 and 0.75 nm^2 are found for calix[4]arene derivatives that contain different numbers of tert butyl groups on their upper rims [7]. Similar research
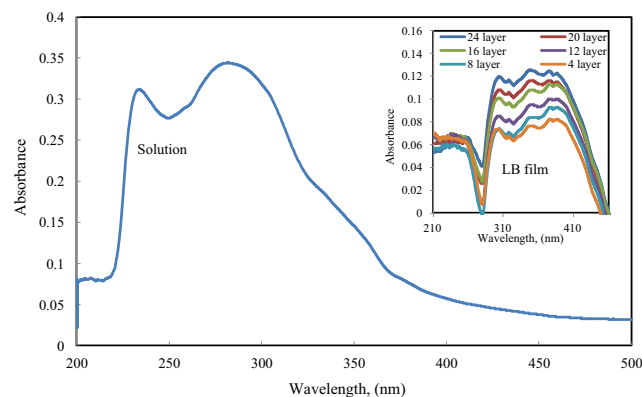

Fig. 3. The UV–vis spectra of a C11TEA solution. Inset: LB film of C11TEA with different numbers of layers.

are found using the method of extrapolating to zero pressure, areas per molecule for calix[4]resorcinarenes between 1.1 nm^2 and 0.75 nm^2 [15]. C11TEA material yields a typical isotherm behaviour with three of the phases as gas (0–1 mN m^{-1}), liquid ($\sim$1–18 mN m^{-1}), and solid phases ($\sim$18–39 mN m^{-1}). The collapse point begins at 39 mN m^{-1} where the order of monolayer is destroyed. This result is supported by McCartney [18]. The area per molecule is strongly dependent on the chemical structure of the materials used and the orientation and packing of molecules at the air–water interface. Several π–A graphs were taken with the same amount of volume value and our results for C11TEA material indicated a good stability and reproducibility.

The efficiency of the LB film deposition is checked 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 described by:

$$\tau = \frac{A_L}{A_S} \tag{3}$$

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. (2), τ is found to be around 0.95. This value can be used to conclude that steady, reproducible and uniform monolayers of C11TEA were deposited from the air–water interface onto a quartz crystal substrate.

3.2. UV–vis spectra of the deposited films

Optical absorption spectrum of C11TEA solution and LB films were recorded in the wavelength range of 200–500 nm. Fig. 3 shows the UV–vis absorption spectrum of C11TEA solution in chloroform and the major absorption peak being observed at 280 nm. This is a typical UV spectra for calixarenes and calixresorcinarenes [1] although substitution can extend the absorption peak, for example azobenzene calixarenes display UV–vis spectra with strong absorption regions around 300–400 nm [19]. The inset in Fig. 3 shows the absorption spectrum of C11TEA LB films with thicknesses between 4 and 24 layers. The UV–vis spectra of the LB films are similar to the solution spectra but UV–vis spectra of the LB films show a wider band (300–400 nm) than that of the one in solution. UV–vis spectrum of the LB film shows a red shift from the UV–vis spectrum of solution this can be due to a number of factors. The nature of the solvent used can affect the resultant spectrum and it is also known that aggregation of molecules can occur in LB films leading to broadening and red-shifting of any adsorption peaks.
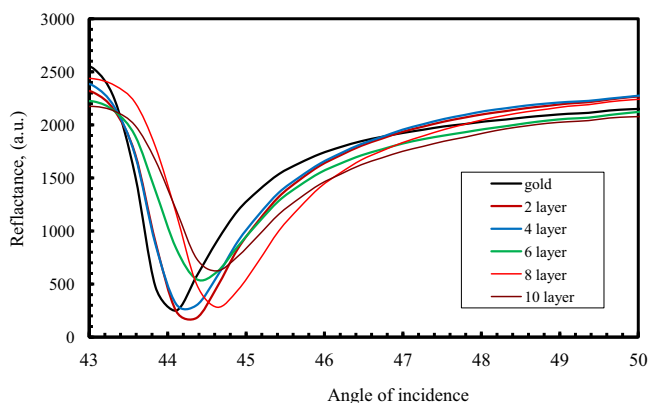
Fig. 4. SPR curves for the C11TEA LB films with different numbers of layers.

3.3. SPR curves and thin film thickness

Fig. 4 shows SPR curve resonance shifts of bare gold and increasing number of layers between 2 and 10 layers of C11TEA LB films. Those curves are shifted to larger angles when number of layers is increased as expected. The film thickness (d) and refractive index (n) of C11TEA LB films were calculated by fitting the SPR curves with a Fresnel formula algorithm via the WINSPALL software as mentioned above. It was assumed that $k = 0$ for C11TEA LB film, since they are transparent at $\lambda = 633$ nm [20]. The fitting calculations produce a mean value of 1.4 for the refractive index of C11TEA LB film. Other studies have determined the refractive index of differing calixarene thin films as 1.494 by [21], 1.48 by [5] and between 1.54 and 1.43 by [22] respectively.

By using the fitting calculations for film thickness demonstrated that when the number of layers is increased, film thickness value is increasing linearly as expected. The average film thickness, determined by the slope of the thickness versus the layer number shown in Fig. 5, is found to be 1.04 nm/deposited layer. The refractive index and thickness of different calixarene materials have been determined to have refractive indexes between 1.47 and 1.70 along with thickness values from 0.80 to 1.50 nm [23]. Capan et al. [24] studied the refractive index and thickness of calix[8]acid LB films and obtained a refractive index value of 1.21 ± 0.08, along with a thickness value (determined by the slope of the thickness versus layer numbers) to be 1.08 ± 0.07 nm/deposited layer.
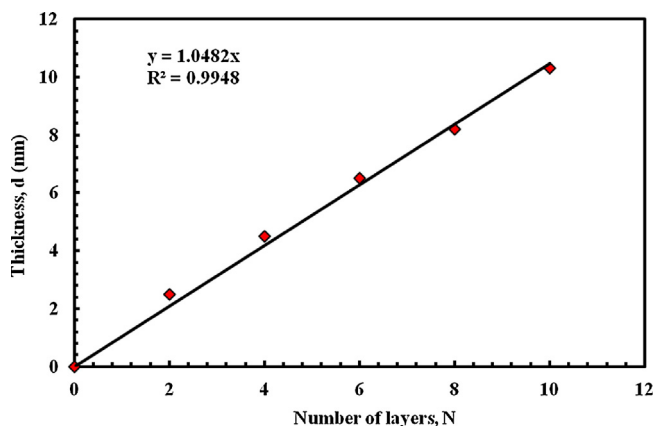

Fig. 5. Thickness of the thin films as a function of the number of layers.
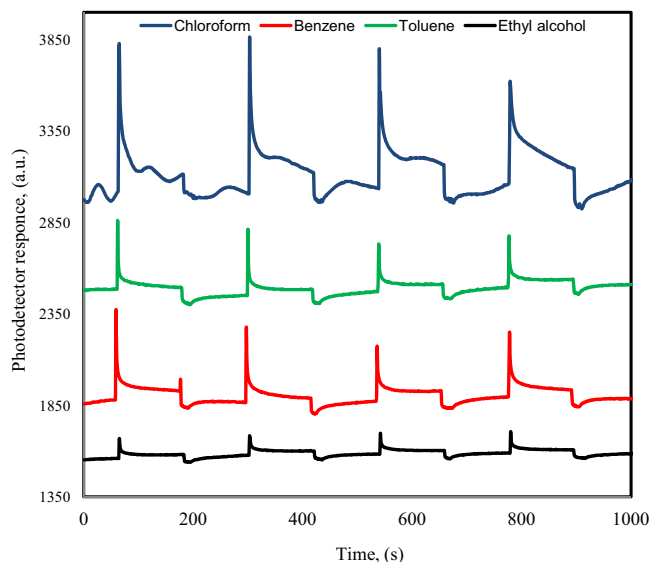

Fig. 6. Kinetic response of sensor coated with C11TEA (10 layers) to injection of vapours into the working cell.

3.4. Organic vapor sensing properties

It is important to understand the response properties between the C11TEA molecule and organic vapours to allow for the detection and identification of organic vapor for application as room temperature vapor sensors. In the SPR vapor sensing arrangement, usually, a photodiode operates as a detector providing an output voltage proportional incident light intensity. The measurement angle is fixed at a point on the steepest part of the resonance curve and the photodiode output is a monitored as a function of time. This is called a kinetic measurement. The kinetic responses of the C11TEA LB film to the chloroform, benzene, toluene and ethyl alcohol vapours is given in Fig. 6 by measuring the reflected light intensity as a function of time for 2 min, followed by injection of dry air for a further 2 min period.

The kinetic responses of the C11TEA LB film in the form of light intensity change to all vapours are almost reversible. Their response and recovery times are given in Table 1. Their values are in the order of a few seconds when the gas cell is flushed with dry air. The first stage in VOC analysis is to flush a reference gas (dry air) through the sensor to obtain a baseline (I_0). When the LB film sensor material is exposed to the organic vapor, this causes changes in the output signal until the sensor reaches a steady-state (I_1). The vapor is finally flushed out of the sensor using the dry air and the sensor response returns back to its baseline. The time during which the sensor is exposed to the vapor is called "the response time" while the time it takes the sensor to return to its baseline resistance is "the recovery time". ΔI indicates the degree of the total response of C11TEA LB film which is the difference between the observed light intensity response (I_1) and the baseline light intensity (I_0). Table 1 summarizes the analysis of kinetic responses. Here, C11TEA LB film shows a fast response as well as a fine degree of recovery, with response and recovery times typically of a few seconds. This process is repeated four times and each vapor gives similar responses to their initial response. For a reproducible and reliable 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 C11TEA LB film yielded a relatively stable repeatability, a good reproducibility, and almost uniform changes in reflected light intensity due to the adsorption and desorption processes. It can be used several times for the detection of these vapours. The total responses of

Table 2
Analysis data of the kinetic response of C11TEA LB film.

	Cycle	Response time (s)	Recovery time (s)	I_0 (a.u.)	I_1 (a.u.)	ΔI $[I_1 - I_0]$ (a.u.)	The mean value $\bar{I} = \frac{\sum_{i=1}^{n} \Delta I_i}{n}$	Standard deviation $\sigma = \sqrt{\frac{\sum_{i=1}^{n}(\Delta I - \bar{I})^2}{(n-1)}}$
Chloroform	1	2	3.5	2972.04	3114.12	142.08	159.85	± 12.07
	2	1.5	3.7	3008.52	3177.48	168.96		
	3	1.3	3.4	3035.40	3200.52	165.12		
	4	3.9	7.3	3056.52	3219.72	163.20		
Benzene	1	1.1	2.5	1853.54	1927.61	74.07	79.27	± 4.86
	2	1.2	2.8	1811.88	1888.26	76.38		
	3	2.0	3.4	1844.29	1926.45	82.16		
	4	2.5	5.6	1850.07	1934.55	84.48		
Toluene	1	1.4	4.3	2421.32	2494.77	73.45	67.50	± 5.49
	2	1.4	4.5	2419.25	2484.43	65.18		
	3	2.2	3.5	2449.25	2510.29	61.04		
	4	2.1	3.9	2467.87	2538.22	70.35		
Ethyl alcohol	1	1.2	1.7	1544.74	1580.43	35.69	37.11	± 1.65
	2	1.8	2.2	1561.81	1600.60	38.79		
	3	1.7	2.8	1567.50	1603.19	35.69		
	4	2.3	4.5	1569.05	1607.33	38.28		

C11TEA LB film for the organic vapours in the following ascending order are: chloroform > benzene > toluene > ethyl alcohol. This calixresorcinarene is more selective to chloroform vapor than towards the other vapours. A similar work reported that the exposure of chloroform vapor is more effective than benzene on the optical parameters of spun film because of the interaction in the form of CH–π bonding between chloroform vapor and the electron-rich aromatic rings of the calixresorcinarene thin films [25]. Benzene vapor shows a higher response that toluene vapor; however both of them have benzene rings. It is well known that the number of adsorbed benzene vapours is higher than toluene vapours because benzene is more volatile, has a lower molar volume and a relatively high viscosity parameter, indicating that benzene molecules are more mobile than the toluene vapours and penetrate easily into the C11TEA LB film structure [7]. A number of other calixarenes have previously been reported to show similar sensitivity towards chloroform [26,27] (Table 2).

4. Conclusion

C11TEA molecule was investigated in the form of LB thin films using UV–vis and SPR measurements. Isotherm analysis indicated that a stable and reproducible monolayer of the material was formed in the air–water interface. The limiting area per molecule was shown to have a value of 1.79 nm^2 and a uniform LB deposition was observed with a transfer ratio of $\geq$95%. The UV–vis spectra of the LB films are similar to the material spectra in chloroform solution albeit with some broadening and red-shift in the solid form, possibly due to aggregation. The thin film thickness (1.04 nm/layer) and refractive index value (1.4) was obtained using SPR curves. SPR kinetic measurements show that C11TEA LB films were significantly sensitive to chloroform and the response of the film is fast, large, reproducible and had a short recovery time, typically of a few seconds. The total response of the C11TEA LB film for the organic vapours is in the following ascending order: chloroform > benzene > toluene > ethyl alcohol. These results demonstrate the possibilities for the development of optical sensors for C11TEA films.

Acknowledgement

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