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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.

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 physicochemical 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 MΩ 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 $AlCl_3$ 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 $AlCl_3$ 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 K_2CO_3 as base. The subsequent Friedel–Crafts deterbutylation step was carried out in toluene using $AlCl_3$, 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 $ArCH_2Ar$, 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 $172\ mm^2\ min^{-1}$.

As shown in Fig. 2, an extrapolation of the linear part produces the values of area per molecule in the condensed state ($1.71\ nm^2$, $1.21\ nm^2$, $1.19\ nm^2$ and $0.75\ nm^2$ 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 $1–2\ nm^2$ reported for similarly sized calixarenes with different side chains [46–48]. The area per molecule values found in this work closely agree with