Characterization of a Novel 1,3-Bis(\(\rho\)-iminobenzoic acid)indane Langmuir-Blodgett Film for Organic Vapor Sensing

R. Çapan,¹* M. Evyapan,¹ H. Namli,² O. Turhan,² and G. A. Stanciu³

¹Physics Department and ²Chemistry Department, Balkesir University, Science Faculty, 10100 Balkesir, Turkey
³Center of Microscopy-Microanalysis and Information Processing, University 'Politehnica' of Bucharest, 313 Splaiul Independenței, 060032 Bucharest, Romania

In the present paper we report about the Langmuir-Blodgett thin film characterization and organic vapor sensing properties of a novel 1,3-bis(\(\rho\)-iminobenzoic acid)indane (IBI) containing polar carboxylic acid groups. LB film properties of IBI material is characterized by UV-visible spectroscopy, atomic force microscopy, and quartz crystal microbalance. Our results show that high-quality and uniform LB films can be prepared with the transfer ratio of over 0.95. Organic vapor sensing properties are studied using quartz crystal microbalance measurement system. IBI film is found to be significantly more sensitive to benzene and the response of LB sample is fast, large, and reversible. The sensitivity of detection of toluene, ethyl alcohol, and isopropyl alcohol is much smaller than that of benzene. This newly synthesized IBI is a suitable molecule for the fabrication of an LB film and can be regarded as a promising sensing material in the development of a room temperature gas sensor for benzene vapor applications.

**Keywords:** Langmuir-Blodgett Thin Film, 1,3-Bis(\(\rho\)-iminobenzoic acid)indane, Organic Vapor Sensing, Quartz Crystal Microbalance.

1. INTRODUCTION

Different types of organic materials were extensively studied using several thin film deposition techniques for their gas sensing properties such as porphyrin,¹,² calixarene,³–⁵ phthalocyanine,⁶,⁷ poly(methyl methacrylate),⁸ polysiloxane,⁹,¹⁰ poly(3-butoxythiophene) mixed with stearic acid,¹¹ 5,5′-methylenebis(\(N\)-hexadecylsali-cylideneamine).¹²

There is not much information in the literature on the study of indanedione-based materials as a gas sensing application using thin film deposition techniques. However, several indanedione materials are studied for electrical properties,¹³,¹⁴ second harmonic generation,¹⁵–¹⁷ and photonics applications.¹⁸ Novel red electroluminescent (EL) materials using indanedione derivatives were designed and synthesized for emission layer in EL devices by Kim.¹⁹

A new type of intermolecular charge-transfer dye incorporating indanedione molecules is studied for its optical properties.²⁰ 2-(\(p\)-N-Hexadecyl-\(N\)-methylamino) benzylidene-1,3-indanedione is used to the preparation of nonlinear optically active Langmuir-Blodgett layers, and UV-visible spectra indicate that a successive uniform LB film layer was prepared for the investigation of second harmonic generation.¹⁷ Similar investigations using Langmuir-Blodgett thin film deposition techniques have been studied for amphiphilic indanedione-1,3 pyridinium betaine by several researchers.¹⁵,¹⁶,²¹ Another good example of the potential application for indanediones is photoinduced intramolecular electron transfer, studied with a 1,3-indanedione anion and a N-pyridinium cation LB film designed as an electron donor/acceptor system.²²

In the present work, LB film characterization of a novel 1,3-bis(\(\rho\)-iminobenzoic acid)indane (IBI) material will be reported using UV-visible, AFM, and QCM measurements. The organic vapor sensing properties of an LB film using

*Author to whom correspondence should be addressed.
an indanedione material have been observed will be given here.

2. EXPERIMENTAL DETAILS

IBI was synthesized using 1,3-indanedione and p-amino-benzoic acid in hexane with a catalytic amount of glacial acetic acid, and the chemical structure of IBI material is shown in Figure 1. IBI was dissolved in a 9 : 1 ratio of chloroform and methanol. The solution, 0.5 mg ml⁻¹, was used to take an isotherm and to produce an LB film by spreading on the pure water surface. 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 of IBI was recorded as a function of surface area at pH 6.0, and the compression speed for the monolayer was controlled at 1000 mm min⁻¹. The isotherm graph was repeated several times, and the results were found to be reproducible. The temperature of the water subphase was controlled by using a Lauda Ecoline RE 204 model temperature control unit, and all experimental data were taken at room temperature.

LB film deposition on a glass substrate for UV-visible and AFM, on a quartz crystal for QCM measurements was performed at room temperature on a NIMA LB Trough 622 type (Coventry, England) with an area of 1200 cm². The different numbers of monolayer were deposited on these substrates under a pressure of 22.5 mN m⁻¹. The deposition mode for the LB film was Y-type. The UV-visible spectra of LB films were recorded in the ultraviolet and visible spectral region from 250 to 800 nm using a VARIAN CARY 1E UV-visible spectrophotometer in the absorbance mode. Atomic force microscopy analysis was performed by using a Quesant 350 scanning probe microscope. The scale is set in such a way that light colors correspond to higher structures. The images were taken by using a standard silicon nitride tip (constant force 12 N/m) in the contact mode.

A thinly cut wafer of raw quartz sandwiched between two electrodes in an overlapping keyhole design was used for the QCM measurements and is shown in Figure 2. QCM measurements were performed at room temperature using an in-house designed oscillating circuit and standard quartz crystal with a nominal resonance frequency of 9 MHz. The frequency was measured with a MOTECH FG-513 model function generator and TEKTRONIX TDS 210 model digital oscilloscope.

3. EXPERIMENTAL RESULTS

3.1. Langmuir Characterization

The measurements of the surface pressure-area (Π-A) isotherms were carried out by the use of a Langmuir trough with a Wilhelmy-type balance. The Π-A isotherm graph of IBI was obtained by reducing the surface area and is shown in Figure 3. The surface pressure starts rising at an area around 0.8 nm² and gradually increases upon compression until the surface pressure rises to nearly 32 mN m⁻¹ when collapse of the monolayer occurs.

3.2. Deposition Process

From the analysis of the isotherm, a surface pressure of 22.5 mN m⁻¹ was chosen for all deposition processes and the transfer ratio is ~0.95 for Y-type LB films deposited onto glass and the QCM substrates. These results indicate that a stable monolayer of IBI formed on the water sub-phase and a uniform LB deposition occurred onto a glass or QCM crystal substrates.

Figure 4 shows typical UV-visible absorption spectra of a solution in mixture of 90% of chloroform and 10% methanol. The solution exhibits absorption bands at 314, 382, and 590 nm. The absorption peak at 314 nm is from
the aromatic $\pi-\pi^*$ transition and the other two peaks with lower intensities are related to $\pi-\pi^*$ and $n-\pi^*$ transitions from the imine structure (C=N) of the IBI molecule.

Figure 5 displays the UV-visible absorption spectra of the IBI LB films with different numbers of layers, in which three obvious bands at 280, 400, and 615 nm are associated with electronic transitions within the molecular structure. When the number of layers increased, the wavelength of the absorption peaks of the LB films remained unchanged, while the intensities of the absorption peaks increased. The absorbance peaks taken from LB films have a similar feature to the absorbance peaks for the solution.

A linear dependence of the absorbance on the number of layers can be obtained, indicating the reproducible film deposition onto glass substrate. The inset in Figure 5 shows a plot of the absorbance at 615 nm of the deposited LB films versus the number of LB film layers. The three points indicate a trend for a linear increase, which is actually confirmed with the QCM data. In the latter, indeed it is shown that the amount of material deposited is the same in each deposition step.

In an attempt to determine the quality of LB film multilayers on the QCM crystal, the relationship between the frequency change and mass change is investigated. A quartz crystal with electrodes on both sides will resonate at an extremely well-defined frequency when placed in a suitable electronic control unit. The resonant frequency depends on the area of the electrode and thickness of the quartz crystal. The resonant frequency of the crystal is extremely sensitive to small mass changes. The change in resonant frequency, $\Delta f$, has been shown to be directly proportional to the mass deposition on the quartz crystal and this relation can be given by

$$\Delta f = \frac{2f_0^2 \Delta m}{\rho_q v_q A}$$

(1)

where $f_0$ is the initial oscillation frequency, $\rho_q$ is the density of piezoelectric slab, $v_q$ is the propagation speed of acoustic waves in the quartz, $\Delta m$ is the change in mass associated with the deposition, and $A$ is the electrode area.

In LB films, $\Delta f$ should be related directly to the mass of the bilayer and the change in resonant frequency for LB films may be written by

$$\Delta f = \frac{2f_0^2 \Delta m}{K_q N}$$

(2)

where $N$ is the number of deposition layers, $\Delta m$ is the mass per unit area per layer, and $K_q = \rho_q v_q$. It is clear that the linear relationship confirms that the transfer process of the LB film is highly reproducible. Figure 6 shows a plot of the change in the resonant frequency against the number of deposited layers for IBI LB film. From the Figure 6, this linear relationship suggests that equal mass per unit area is deposited onto the quartz crystal during the transfer.
of each bilayer. The gradient of this graph shows that the typical frequency shift, $\Delta f$, is $\sim 194$ Hz per bilayer. The mass deposited on the quartz crystal per bilayer can be calculated as $224$ ng by using Eq. 2.

The morphological examination of IBI LB film was carried out using atomic force microscope in contact mode. Figure 7 depicts an atomic force microscope image of a 15 layer IBI assembly deposited at a rate of $1000$ mm min$^{-1}$ onto an optically flat hydrophilic glass substrate. LB film exhibited a smooth, compact, uniform, and void-free morphology with a root-mean-square (rms) value between $0.3$ and $0.5$ nm. This measurement was repeated using LB film samples with a different number of layers and the surface roughness of the film increases when the number of layer increased. The thickness obtained from AFM measurements is almost linearly increasing with the number of layers. The thickness per layer for IBI LB films is obtained in the range $1.5$–$2.5$ nm using an AFM picture and the molecular thickness of IBI is calculated as $1.8$ nm by using Corey-Pauling-Koltun (CPK) model.

### 3.3. Organic Vapor Properties

The kinetic response of the LB sample to the benzene ($C_6H_6$), toluene ($C_7H_8$), ethyl alcohol ($C_2H_5OH$), and isopropyl alcohol ($C_3H_7O$) vapors was recorded by measuring the frequency changes. Figure 8 shows the variation of the frequency changes as a function of time when the sample was periodically exposed to the organic vapors for $2$ min followed by the injection of dry air for a further $2$ min period. The LB film sample from IBI material is found to be significantly more sensitive to benzene vapor than other organic vapors, and as soon as air was injected to the gas cell, the LB sample was found to recover almost fully. The response in terms of frequency changes in the graph to the exposure of benzene vapor is fast, large, and
reproducible, and full recovery was observed after flushing the gas cell with fresh air, the facts typically observed for adsorption of organic vapors of high concentration in IBI LB film. Values of $\Delta f$, which indicates the degree of response, are measured with an accuracy of 1% Hz. The change in frequency is altered by 41% when benzene is present and similar calculations were carried out for the other vapors shown in Figure 9. According to the degree of frequency change, IBI is reasonably selective for benzene. Benzene is a nonpolar solvent and toluene, ethyl alcohol, and isopropyl alcohol are expected to show stronger solvation than benzene.

4. CONCLUSION

Novel 1,3-Bis($p$-iminobenzoic acid)indane molecules were successfully deposited onto glass and quartz crystal substrates by Langmuir-Blodgett thin film deposition technique. UV-visible, AFM, and QCM results show that a high quality and uniform LB film is produced with a transfer ratio of over 0.95. IBI film is found to be significantly more sensitive to benzene vapor than other vapors. The response in terms of frequency change to the exposure of benzene vapor is fast, large, and reversible. The IBI LB film may find potential applications in the development of room temperature gas sensors for benzene vapor.

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References and Notes


Nano-Devitrification of Glassy Alloys - REVIEW
Water-Photolysis by Highly-Ordered Titania Nanotube Arrays
DNA Wrapped HiPco Carbon Nanotubes
Sub-100 nm Lithography
ZnO Nanowires