

Fabrication of a novel 1,3-bis(*p*-hydrazonobenzoic acid)indane Langmuir–Blodgett film and organic vapor sensing properties

M. Evyapan^a, R. Çapan^{a,*}, H. Namlı^b, O. Turhan^b

^a Balıkesir University, Science Faculty, Physics Department, 10145 Çağış/Balıkesir, Turkey

^b Balıkesir University, Science Faculty, Chemistry Department, 10145 Çağış/Balıkesir, Turkey

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Abstract

A novel 1,3-bis(*p*-hydrazonobenzoic acid)indane (HBI) molecule was synthesised for the study of monolayer properties at the air–water interface, the fabrication of a Langmuir–Blodgett film, and the investigation of organic vapor sensing properties. Langmuir properties of HBI were studied by taking an isotherm graph. Two different surface pressures were selected for the fabrication of multilayer LB films that were deposited onto glass and quartz crystal substrates.

UV–vis spectroscopy and a quartz crystal microbalance (QCM) measurement system were employed to monitor the deposition quality under the two selected deposition pressures. Our results showed that a uniform and high quality LB film with a transfer ratio of 0.96 occurred using the HBI material at a deposition pressure of 22.5 mN m⁻¹.

The LB film deposited onto the quartz crystal was used to study the interaction of the HBI material with different organic vapors such as chloroform, benzene, toluene, ethyl alcohol and isopropyl alcohol. Our results show that the HBI material is suitable to produce an organic thin LB film. Our results indicate that the HBI LB film is highly sensitive to chloroform vapor with a fast and reversible response. This new HBI material could be used as a vapor sensing material.

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Keywords: Langmuir–Blodgett film; Organic vapor sensing; Quartz crystal microbalance

1. Introduction

A large number of organic materials were used to study their optical and electrical properties [1,2], interlayer electron transfer [3], photoconductivity [4], organic light-emitting diodes [5] and sensor applications [6,7]. Several organic materials such as porphyrin [8,9], calixarene [10,11], phthalocyanine [12,13], poly(methyl methacrylate) [14] were extensively studied in the field of gas sensing applications. A limited study in the literature has been done on the study of indandione-based materials as a gas sensor [7]. However, other properties of indandione-based materials such as electrical [15], second harmonic generation [16] and photonics [17] were studied using different thin film

deposition techniques. Indandione materials were also used for biological effects [18,19]. Successive Langmuir–Blodgett (LB) films using 2-(*p*-*N*-hexadecyl-*N*-methylamino)benzylidene-1,3-indandione were prepared for investigation of non-linear optical properties [20]. Amphiphilic indandione-1,3 pyridinium betaine material was used to produce an LB film for investigation of physical properties [21]. The photoinduced intramolecular electron transfer mechanism was studied using a 1,3-indandione anion and an *N*-pyridinium cation as electron donor/acceptor system [22]. These results show that indandione and its derivatives are candidate materials to produce an LB film for the study of their physical and sensing properties.

In this work, a novel 1,3-bis(*p*-hydrazonobenzoic acid)indane (HBI) material was selected to study the LB film characteristics and organic vapor sensing properties. An alternate layer LB trough, a UV–vis spectrophotometer and a quartz crystal microbalance (QCM) measurement system were employed to

* Corresponding author. Tel.: +90 266 612 10 00; fax: +90 266 612 12 15.
E-mail address: rcapan@balikesir.edu.tr (R. Çapan).

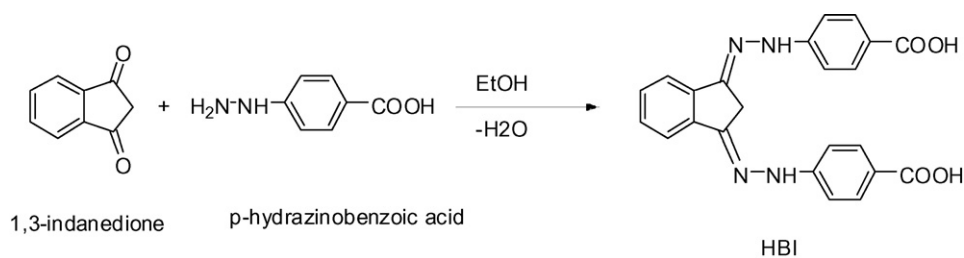


Fig. 1. Synthesis route and molecular structure of HBI.

investigate these properties of the HBI material. In addition, the organic vapor sensing properties of this LB sample using HBI were reported for the first time.

2. Experimental details

HBI was synthesized from the condensation reaction of 1,3-indanedione and *p*-hydrazinobenzoic acid. 0.29 g of 1,3-indanedione and 0.76 g of *p*-hydrazinobenzoic acid were mixed in an ethanol solution and it was stirred 2 days at room temperature. While both reagents were soluble in ethanol, the crude precipitate was filtered off (0.87 g, yield 83%) and then recrystallized in dioxane for purification (0.63 g, yield 60%). The synthesis route and molecular structure of HBI is shown in Fig. 1.

The HBI solution was dissolved in chloroform and dimethylsulfoxide (DMSO) (9:1) at a concentration of 0.1 mg ml^{-1} before being spread onto the distilled pure water surface in a computer controlled Nima 622 LB Trough (Coventry England) at pH 6.0. A Lauda Ecoline RE204 model temperature control unit was connected to the LB trough to control the temperature of the water subphase. All measurements were carried out at room temperature. After waiting for 15 min, the Π -A isotherm of HBI was recorded as a function of a reduced surface area. The isotherm graph was taken several times and was found reproducible. The LB film monolayers were deposited onto a glass and a quartz crystal substrate by a vertical dipping method using a speed of 10 mm min^{-1} . The LB film deposited onto a glass

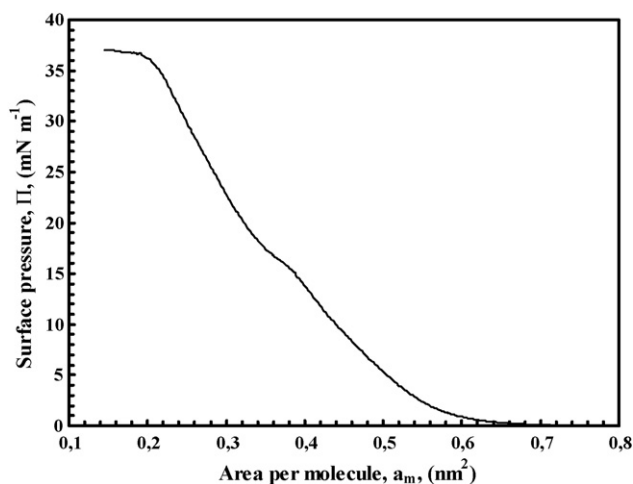


Fig. 2. Isotherm graph of HBI.

substrate was characterized by using a Varian Cary 1E UV–vis spectrophotometer in a region from 350 and 700 nm. A QCM system was used to monitor the deposition of the LB film layers and to display the kinetic response of the LB sample against different organic vapors. The QCM system [6] consisted of a thinly AT cut quartz crystal sandwiched between two electrodes with a 9 MHz frequency. A special gas cell was constructed to study the response kinetics of the HBI LB films on exposure to organic vapors by measuring the frequency changes. The frequency changes were monitored as a function of time, when the sample was periodically exposed to organic vapors at least for 2 min, and was then allowed to recover after injection of dry air. The frequency was measured with a MOTTECH FG-513 model function generator and a TEKTRONIX TDS 210 model digital oscilloscope.

3. Results and discussion

Fig. 2 shows the surface pressure area or isotherm graph of HBI. The HBI monolayer at the air–water interface shows a phase transition between 15 and 17 mN m^{-1} , which could be caused by the transformation of molecular shape during compression of the monolayer at the water surface [23]. The monolayer of HBI starts to collapse around 35 mN m^{-1} . The deposition pressures of 9 and 22.5 mN m^{-1} were selected to produce LB films onto a glass substrate. From the isotherm graph

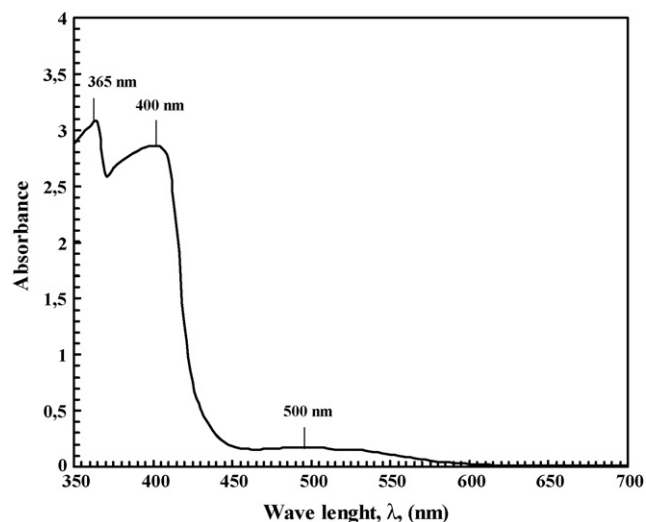


Fig. 3. UV–vis absorption spectrum of HBI of 0.1 mg ml^{-1} in a mixed solution of chloroform and DMSO.

the area per molecule of HBI was determined to be 0.45 nm^2 for 9 mN m^{-1} and 0.3 nm^2 for 22.5 mN m^{-1} , respectively.

Fig. 3 shows the UV–vis spectrum of HBI in a mixed solution of chloroform and DMSO (9:1). The absorption peak at 365 nm occurs from the aromatic $\pi-\pi^*$ transition [22–24] and other peaks at 400 and 500 nm are related to the $\pi-\pi^*$ and $n-\pi^*$ transitions from the imine structure ($\text{C}=\text{N}$) of the HBI molecule [25,26]. Fig. 4 gives the UV–vis spectra of LB films using a different number of layers. The UV–vis spectra of the LB films are similar to the HBI spectrum of the solution form, except that the bands at 365 and 400 nm are broadened and the other band at 500 nm in the solution spectrum is red shifted by about 10 nm . This might be explained by the occurrence of molecular aggregation in the LB films [27,28]. Similar red shift is observed for a 1,3-bis-(*p*-iminobenzoic acid)indane Langmuir–Blodgett film [7].

The absorption intensity increased when the number of layers increased. The inset in Fig. 4 shows variations of absorption intensity at 385 and 510 nm as a function of the number of layers. This linear dependence confirms that the LB film layers can be successfully deposited using the HBI material.

In order to check the transfer process, transfer ratio values were evaluated and found to be 0.55 and 0.96 for the surface pressures of 9 and 22.5 mN m^{-1} , respectively. Thus, the transfer ratio at 22.5 mN m^{-1} was higher than at 9 mN m^{-1} . Therefore, the surface pressure of 22.5 mN m^{-1} was optimized as a deposition pressure in this work. A similar transfer ratio was found for the 1,3-bis-(*p*-iminobenzoic acid) indane LB film material [7].

The quality of an LB film multilayer on a quartz crystal can be checked using the capability of QCM measurement technique. The resonant frequency, Δf , is extremely sensitive to a small mass change that was first discovered by Sauerbrey [29] as given by:

$$\Delta f = \frac{-2f_0^2}{\rho_q^{1/2} \mu_q^{1/2} A} \Delta m \quad (1)$$

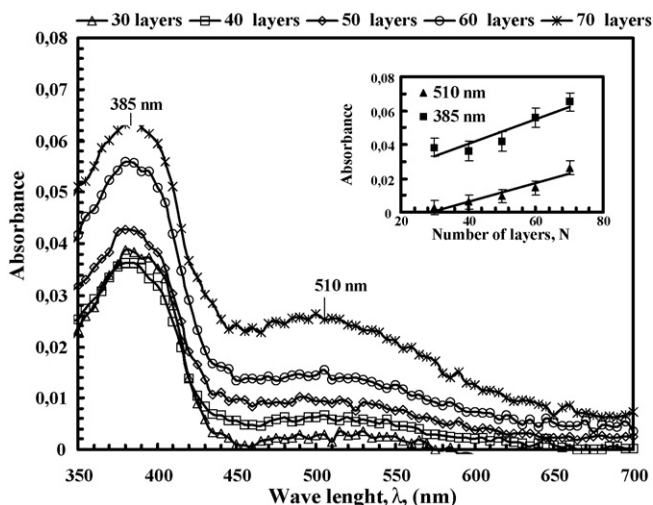


Fig. 4. UV–vis absorption spectra of HBI LB films with a different number of layers.

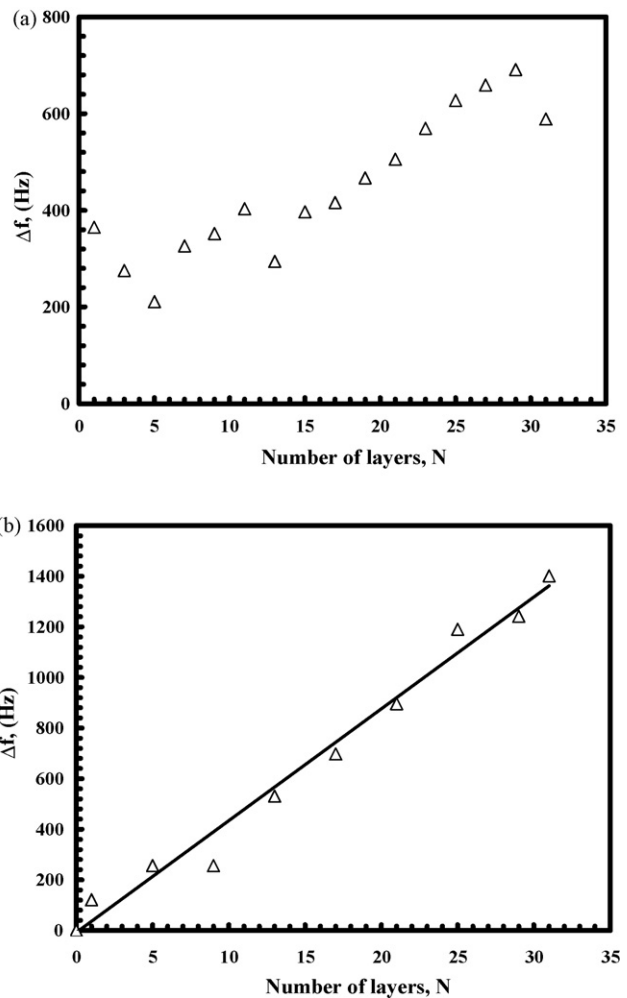


Fig. 5. Changes in resonant frequency vs. the number of layers for two different LB films of (a) 9 mN m^{-1} and (b) 22.5 mN m^{-1} .

where f_0 is the resonant frequency of the fundamental mode of the crystal (Hz), Δm is the mass change (g), A is the piezoelectrically active area (cm^2), ρ_q is the density of quartz (2.648 g cm^{-3}), μ_q is the shear modulus of quartz ($2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$).

Fig. 5 shows the resonant frequency change as a function of the deposited mass using a 9 MHz quartz crystal at two different surface pressure values. Fig. 5a shows the frequency change of the quartz crystal as a function of the number of layers for the surface pressure of 9 mN m^{-1} . The frequency shift versus the deposited mass is not entirely linear because of the poor transfer ratio (0.55) obtained during the deposition process. Fig. 5b gives the relationship between the frequency change and the number of LB film layers at the surface pressure of 22.5 mN m^{-1} . This linear relationship between the frequency and the mass confirms that an equal mass is deposited onto the quartz crystal and a uniform LB film is produced using the HBI material. From the gradient of Fig. 5b and Eq. (1), the typical frequency shift is estimated $\sim 88 \text{ Hz}$ per bilayer and the deposited mass per bilayer is calculated 102 ng . Similar results show that the increasing surface pressure increases the amount of deposited mass [30].

For the detection of organic vapors, several organic materials have been extensively studied due to their fast response, short recovery time, low cost and ease of processing [1,5,13–15]. It is well known that when a vapor molecule is adsorbed on the surface of a material, it may cause a change in the physical, electrical or optical properties of the material. In order to investigate the vapor sensing properties of the HBI LB film, the frequency change is measured towards chloroform (CHCl_3), benzene (C_6H_6), toluene (C_7H_8), ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) and isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$) as a function of time.

Fig. 6 shows the response of the HBI LB film when periodically exposed to the organic vapors for 2 min, followed by injection of dry air for further 2 min. The frequency increased sharply with time at first when the LB film was made contact with the all the vapors. The responses of the HBI LB film were almost reversible with response and recovery times in the order of 10 s when the gas cell was flushed with dry air. All the response measurements of the HBI LB film to organic vapors were run several times, and the results showed that the sensor responses were reproducible. The response of the LB film in the form of frequency change was the largest to chloroform, and on removal of the chloroform vapor the film recovery was similarly fast. This LB film showed 30% less response to alcohols than chloroform. The lowest response was given to benzene and toluene having a benzene ring. It can be concluded that the HBI LB film studied here more or less shows a response to all vapors and is more selective for chloroform than for other vapors. A similar response to chloroform has been reported for the sensors based on different phthalocyanine materials [31,32]. An exposure of the LB film to chloroform vapor yields a large change of the optical parameters of these thin films, and the film thickness increased as a result of film swelling [33]. The reproducibility for all vapors was tested using the kinetic response. The frequency change was recorded as a function of time using several measurements, and the kinetic response indicated that the LB film studied here showed a reversible and reproducible response to all vapors.

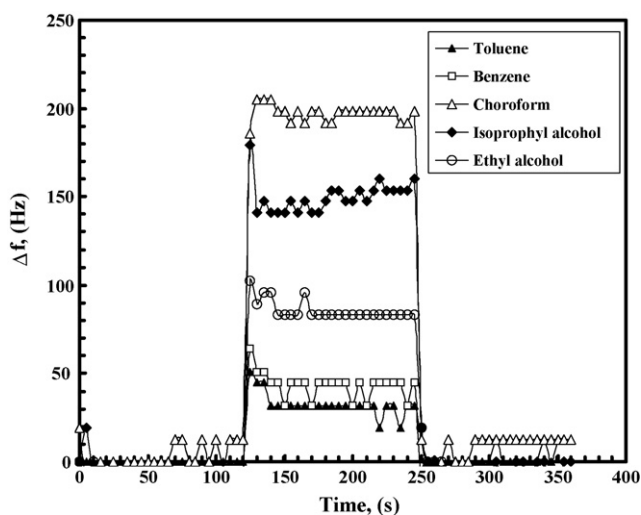


Fig. 6. Frequency shift of an HBI LB film to organic vapors as a function time.

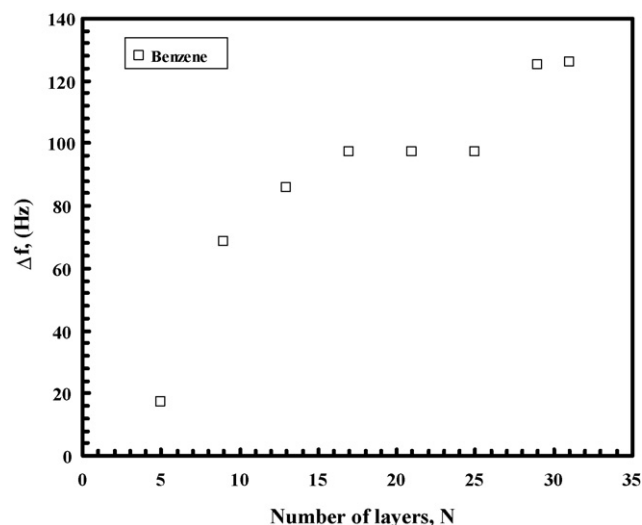


Fig. 7. Frequency shift against benzene vapor vs. the number of layers of the HBI LB films.

To investigate the interlayer vapor diffusion, the HBI LB films with a different number of layers were exposed to benzene vapor. Fig. 7 shows the frequency change as a function of the number of layers. The response increased when the LB film layer was deposited onto the quartz crystal. This could lead to the conclusion that the benzene molecules not only interact with the surface of the HBI sensing material but also can be diffused into the interlayer spaces of the LB film [34,35].

4. Conclusion

The Langmuir properties of a novel 1,3-bis(*p*-hydrazono-benzoic acid)indane (HBI) molecule was investigated at the air–water interface using an isotherm graph. The HBI monolayer at the air–water interface was successfully deposited onto a glass and a quartz substrate at the pressure of 22.5 mN m^{-1} with a transfer ratio of over 0.90. UV–vis and QCM results showed that a high quality and uniform LB film was produced using the HBI material. The HBI LB film sample was found to be sensitive to organic vapors such as chloroform, benzene, toluene, ethyl alcohol and isopropyl alcohol. The response to chloroform vapor was larger than to other vapors. The response was fast and reversible. It can be concluded that this HBI material would be an alternative material to other traditional LB film materials and may find potential applications in the development of room temperature organic vapor sensing devices.

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Biographies

Murat Evyapan received his MSc in physics from the University of Balikesir, Turkey in 2006. He is currently working toward the PhD degree at University of Balikesir, Turkey. He is also a research assistant at the Department of Physics in Balikesir University.

Rifat Çapan received MSc degree at Hacettepe University, Physics Engineering Department, Ankara, Turkey in 1991 and his PhD at the University of Sheffield (UK) in 1998. He established first Langmuir–Blodgett Thin Film Research group in Turkey. His main interests are pyroelectric heat sensor, gas sensor for environment applications, the electrical and optical properties of organic thin film materials. Dr. Capan was appointed assistant professor at University of Balikesir in Turkey in 1999. He became a deputy of Head of Physics Department in 2001 and was the Head of Physics Department between 2003 and 2006. He is currently the director of the Applied Research Centre at Balikesir University. He had a PhD scholarship from Turkish High Education Council between 1993 and 1998 and had Overseas's Research Student award (UK) from 1995 to 1998. Since 2002, he has been working as an associate professor at the University of Balikesir.

Hilmi Namlı has received his MSc degree at Gazi University, Chemistry Department in 1991, Ankara, Turkey and his PhD at the University of Sheffield Department of Chemistry (UK) in 1997. His main interests are the synthesis of organic molecules and characterization of its metal complexes. He also focused on in-situ monitoring of the organic reaction by FTIR. Dr. Namlı was appointed assistant professor at University of Balıkesir department of chemistry in 1998. He had a scholarship from Turkish Higher Education Council

between 1993 and 1997 for his PhD. He has currently been continuing his works as an associate professor at the University of Balıkesir Department of Chemistry.

Onur Turhan has received his MSc at the Department of Chemistry, University of Balıkesir, Turkey. He is currently working as a research assistant and at the same time doing his PhD degree at same University.