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Research Article

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Article Info	Abstract
	LB thin film characterization and vapor sensing applications of 1,7-dibromo-N,N'-(bicyclohexyl)-3,4:9,10- perylendiimide (FY3) materials are reported in this study. The thin film deposition conditions of FY3 materials, which are prepared by LB film technique, are characterized by UV-vis spectroscopy and Quartz Crystal Microbalance (QCM) techniques. The typical frequency shift per layer is obtained as 50.15 Hz / layer and the deposited mass onto a quartz crystal is calculated as 399.36 ng / layer (1.50 ng mm^{-2}). Vapor sensing properties of these LB films against three different volatile organic compounds (chloroform, benzene and toluene) are studied using the QCM technique. The sensitivities to vapors are determined between 3.62 x 10^{-4} and 1.60 x 10^{-4} Hz ppm^{-1}. FY3 LB film is more sensitive to chloroform than other vapors. Responses of the FY3 LB film to these vapors are fast, large and reversible. Detection limits are calculated between 0.83 x 10^4 and 1.88 x 10^4 ppm. It can be concluded that this FY3 material is promising as a vapor sensing device at room temperature.

1. Introduction

In the recent years, chemical sensors have been extensively investigated for possible applications due to their response times, low cost, portability, ease of use and a continuous real time signal. The SnO$_2$-based materials [1], hydrogenated diamond [2], nanocomposite materials [3], p-type oxide semiconductor materials [4], polymers [5], calix[n]arene [6], phthalocyanine [7], porphyrin [8] and perylenes (PDIs) [9] were selected as sensor materials for chemical sensor application. Among them, perylene deritaves are well known organic materials due to their chemical and thermal stability, high optical [10], photophysical and electrochemical properties [11,12]. These materials have been extensively combined in the development of efficient electronic devices as organic solar cells [13], organic light emitting diodes [14], medical applications [15] and gas sensors. The sensing properties of perylene–adamantane nanocomposite thin films were investigated for NO$_2$. These thin films showed promising results for the development of accumulative sensors of NO$_2$ [16]. Three perylenediimide derivatives PTCDI-Br$_2$C$_{10}$,

PTCDI-C_{10} and PTCDI-BP_2C_{10} were investigated their sensing properties against to the hydrazine vapor [17]. Zang and his group fabricated a sensory materials based on well-defined nanofibers fabricated of hexylheptyl substituted PTCDIs, which has a high sensitivity to organic amines [18]. PTCA-Cys, which comprised of 3,4,9,10-perylenetetracarboxylic acid (PTCA) and L-cysteine (Cys), is prepared as nanostructure film sensor for investigation sensitive detection of ascorbic acid, dopamine and uric acid [19]. The most important process in VOCs identification is the preparation of thin film sensors. There are many methods for thin film fabrication such as casting, spin coating, chemical or physical vapor deposition, and Langmuir-Blodgett (LB) thin film technique. Using LB technique, compared with other coating methods, it is possible to prepare a thin film with a controlled thickness at the molecular level with a well-defined molecular orientation [20]. This technique can offer an effective way to prepare well defined structure of perylendiimide LB film [9], which is promising for chemical sensors device application [21].

In the present work, 1,7-dibromo-N,N'-(bicyclohexyl)-3,4:9,10- perylendiimide (FY3) material is selected to investigate LB thin film characterization and sensing properties against organic vapors such as chloroform ($CHCl_3$), toluene (C_7H_8) and benzene (C_6H_6). Our results showed that the FY3 monolayer are transferred as LB layers onto the QCM crystal or glass substrates with a high transfer ratio. The LB thin film characterization of these layers is monitored by UV-vis and QCM techniques. The vapor sensing measurements were carried out using the QCM system. FY3 material showed very promising results in the vapor sensor application area with a fast, large and reproducible response to chloroform vapor.

2. Experimental Details

The chemical structure of the 1,7-dibromo-N,N'-(bicyclohexyl)-3,4:9,10-perylendiimide (FY3) molecule is shown in Fig. 1. The synthesis process of this material is given in our previous study [22]. Alternate layer Nima 622 model LB film trough provided with a filter paper Wilhemly balance were employed to record the surface pressure–area (Π-A) isotherm graphs and to fabricate the thin films. 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. FY3 was dissolved in chloroform with a concentration of 0.1 mg ml^{-1}. 700 μl solution was spread onto the pure water subphase using a Hamilton syringe allowing approximately 15 min for the solvent to evaporate. After this procedure, the Π-A isotherm of FY3 was recorded with the compression speed of 30 cm^2 min^{-1}. The isotherm graph was taken several times and was found to be reproducible. Π-A graph was used to select the surface pressure value. Monolayers have been transferred at the constant surface pressure value of 22.5 mN m^{-1} onto glass substrates for UV-visible measurement and onto quartz substrates for QCM measurement by the vertical dipping method for QCM and UV-vis measurements.

The UV-vis spectra of LB films were recorded in the ultraviolet and visible spectral region from 320 to 800 nm using an OceanOptics UV–vis light source (DH-2000-BAL Deuterium Tungstenlight source) and spectrometer (USB4000) in absorbance mode. After the deposition of LB film multilayer onto glass substrates, UV–vis measurements carried out with the different number of layers and compared with solution spectra. QCM measurement system was emloyed to monitor the deposition of the LB film layers and to display the kinetic response of the LB sample against different organic vapors
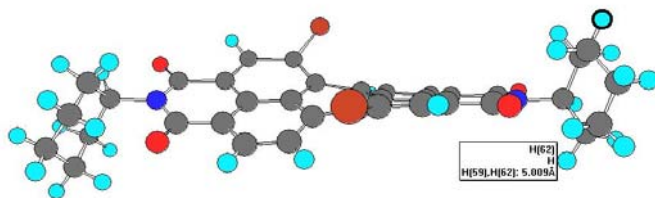
Fig. 1. Chemical structure of FY3 molecule

A block diagram of our home made QCM measurement system is shown in Fig. 2. AT-cut quartz crystal, which is sandwiched between two electrodes in an overlapping keyhole design for QCM measurements, was used. These QCM crystals with a nominal resonance frequency of 7 MHz were commercialized from GTE SYLVANIA Company. All measurements were taken at room temperature (20 °C) using an oscillating circuit that we designed. The quartz crystal was inserted into the electronic control unit, and the frequency of oscillation was monitored as a function of time using dedicated software. The values of frequency changes, which indicate the degree of response, are measured with an accuracy of 1 Hz. After each deposition cycle, the LB film sample was dried for half an hour and the mass change was monitored using this computer controlled QCM measurement system. This system was used for the confirmation of the reproducibility of LB film multilayers using the relationship between the QCM frequency changes against the deposited mass, which should depend on the number of layers in the LB film.
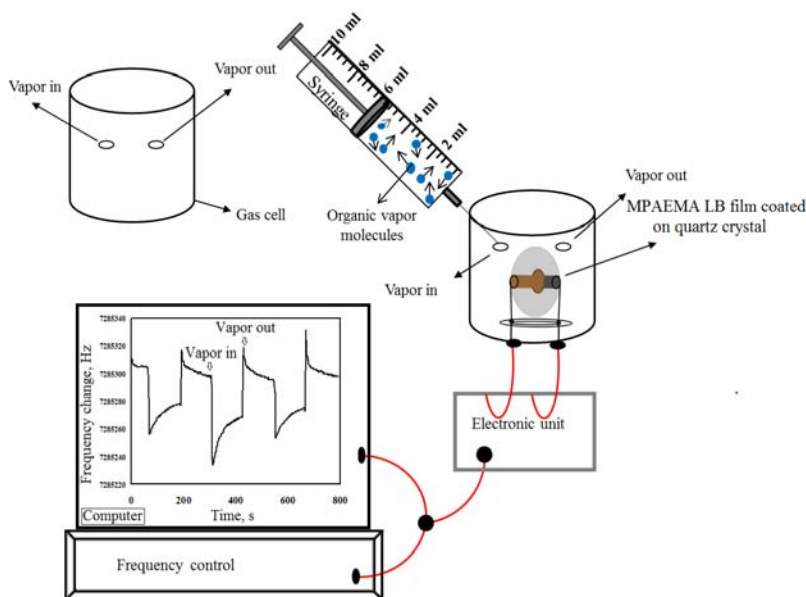
Fig. 2. A block diagram of the quartz crystal microbalance measurement system

A gas cell was constructed to study the LB film response on exposure to organic vapors by measuring the frequency change and these measurements were performed with a syringe. 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 changes in resonance frequency were recorded in real time during exposure to organic vapors. During this procedure the volume

of VOC vapor introduced into the gas cell varied between 2-10 ml. The exposure to VOC vapor for 6 min was followed by flushing of the cell with dry air for another 6 min. This procedure was carried out over several cycles to observe the reproducibility of the LB film sensing element.

3. Results and Discussions

3.1. Fabrication of the Thin Films

LB thin film fabrication parameters including the dipper speed and the surface pressure value that will be held constant during the fabrication need to be determined to fabricate the thin films of perylenediimide. The floating monolayer at water surface was found to be stable at a surface pressure of 22.5 mN m^{-1} that was selected for FY3 LB film deposition procedure. The isotherm graph of this material is given in our previous study [22]. In previous study [22], we also obtained the deposition graph which gives information on the reduction of the surface area of the FY3 monolayer versus dipper position during the deposition of the LB layers onto the substrates.

3.2. QCM measurements

QCM system is used for measuring the resonance frequency of quartz crystal between electrodes which is fairly sensitive to a small mass change at a nanoscale. This measurement technique was first described by Sauerbrey and the resonance frequency change (Δf) on LB film multilayer quartz crystal against a mass change per unit area (Δm) is given by [23]:

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

where, N is the number of deposited LB film layers, Δm is the deposited mass per unit area per layer (g), Δf is the frequency change (Hz), f_0 is the resonant frequency of non-coated quartz crystal (Hz), A is the electrode active area (2.65 cm^2), ρ_q is the density of quartz (2.648 g cm^{-3}) and μ_q is the shear modulus of quartz (2.947x 1011 g cm^{-1} s^{-2}).

Fig. 3 shows the relationship between frequency difference and number of layer during the transfer process of FY3 LB films onto quartz resonators. A systematic change in resonance frequency with the increase in the number of monolayers is clearly observed. This change described Eq. 1 is closely associated with the mass change of LB layers on the substrate and is highly reproducible and uniform. It also suggests that equal mass per unit area is deposited onto the quartz crystal during the transfer of LB film layers. Typical frequency shift of 50.15 Hz / per layer for FY3 LB film is obtained from the slope of the plot. The mass deposited on the quartz crystal per bilayer is estimated as 399.36 ng (1.50 ng mm^{-2}) for FY3 LB film using Eq. 1 and Fig. 3.
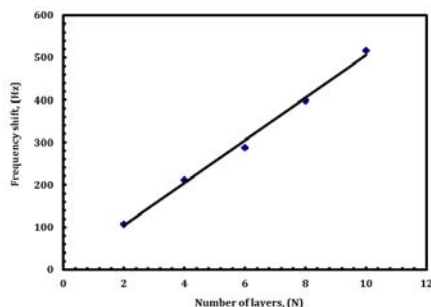

Fig. 3. The transfer graph of FY3 LB film on the quartz crystal

3.3. UV-Visible Results

Fig. 4 displays UV-vis absorption spectra of a FY3 solution in chloroform with a concentration of ~0.1 mg ml^{-1}. The solution spectrum exhibits four absorption peaks at 393, 462, 495 and 528 nm. They are similar to a progression of π-π* transitions of perylene ring and are in good agreement with the literature values taken with other perylene materials [24]. Perylenediimides exhibit strong absorption of light in the wavelength range 450-550 nm and near unity quantum yield of fluorescence between 540 and 620 nm [25]. The optical absorption characteristics of 3,4,9,10-perylenebis(dicarboximide)s with varying the substituent on the imide functions such as pyrrolidinyl, piperidyl, and morpholinyl groups were studied to investigate the effect of these groups on the perylene nucleus. The results showed that the optical absorption characteristics of perylenediimides are highly dependent on the varying substituent on the imide functions [26].
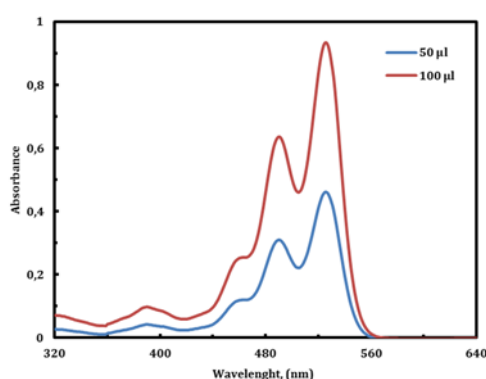
Fig. 4. UV-vis spectra of FY3 in a chloroform solution. (Peaks are 393, 462, 495 and 528 nm.)
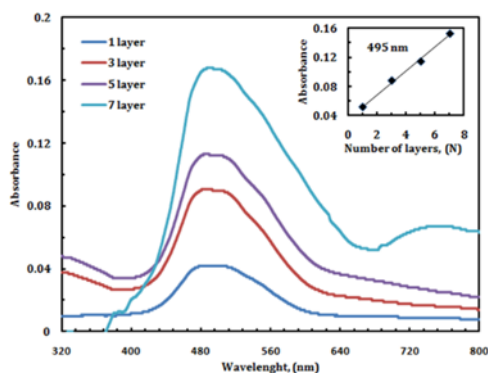
Fig. 5. UV-vis spectra of FY3 film. (The inset: absorbance as a function of number of layers at 495 nm.)

Fig. 5 displays UV-vis absorption spectra of FY3 LB films transferred onto a glass substrate with different layer. The absorption intensity increased when the number of layers increased. In order to monitor the deposition of FY3 LB film layer onto the glass substrate, the relationship between the absorbance and mass deposition is investigated. The inset in

Fig. 5 shows variations of absorption intensity at 495 nm as a function of number of layers. This linear relationship confirms a fairly constant mass ratio during sequential dipping of the substrate through the LB monolayer. This demonstrates successful adhesion of the monolayers onto the glass substrate.

3.4. Gas Measurements of FY3 LB Film

In order to study the potential application of FY3 LB film in the field of vapor sensing, the kinetic response of the LB sample to chloroform, benzene and toluene vapors is recorded by measuring the frequency changes as a function of time. FY3 LB film is periodically exposed to the organic vapors for 6 min, followed by the injection of dry air for a further 6 min period. Fig. 6 displays the mechanism of gas permeation into the sensing material. In the initial step, FY3 LB film sensor expose to dry air for nearly 360 seconds and the response was a stable value in this period of time. The initial response of FY3 LB film in the QCM system for all vapors increased sharply between 360 and 365s due to surface adsorption effect. When the vapor molecules moved into the FY3 LB film sensor, the response decreased exponentially, which resulted from bulk diffusion effect. In the 720s, after flushing dry air, a rapid decrease of response was observed and then recovery process occurred between 720 and 724s for all vapors due to desorption of vapor. After 725s, the response of FY3 LB film sensor reached a stable value and the sensor obtained initial baseline. As a result, response of the LB thin film to these organic vapors is fast, reproducible and reversible.

Fig. 7 shows the kinetic response of the FY3 LB film sensor to different volumes of chloroform. This sensor is exposed to a certain volume of chloroform gas (2.78×10^4-13.91×10^4 ppm) and it is clearly that the frequency shift increases when the volume of chloroform is increased. Fig. 8 gives the typical frequency-response of the FY3 LB film to organic vapors at room temperature. It can be seen that as the concentration of the percentage increases, the frequency shifts increases proportionately. The frequency shifts of FY3 LB thin film sensor versus the volumes of the three VOCs are plotted and shown in Fig. 9. It is found that with the enhancement of gas volume, the frequency shift increases and gives an almost linear response to gas volume for chloroform, benzene and toluene.
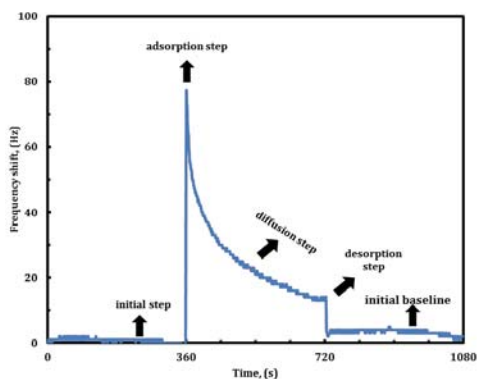

Fig. 6. The mechanism of gas permeation into the sensing material

The limit of detection (LOD) of the FY3 LB film sensor was calculated by the measured sensor sensitivity (Hz / ppm). LOD was defined by [27]:

$$LOD = 3\sigma/S \qquad (2)$$

where, σ is the noise level of the fabricated QCM sensor, and S is the sensitivity to a specific analyte of the sensor. The sensitivity of LB film sensor was obtained from the frequency shift curves when exposed to organic vapors in Fig. 9. The approximate values of the curves were obtained from this figure. The frequency noise of QCM system was estimated at 1 Hz by recording the absolute frequency of quartz crystal. The sensitivity and detection performance of the fabricated QCM sensor to several volatile organic vapors is given in Table 1. The FY3-coated QCM sensor displayed sensitivity with detection limits of 0.83 x 10^4 and 1.88 x 10^4 ppm for various organic vapors at room temperature. QCM results in this study showed that chloroform produce the largest sensitivity value (3.62 x 10^{-4} Hz ppm^{-1}). VOCs molecules enter into the perylendiimide chains and expand the volume of chain causing swelling. The values of sensitivity are found as chloroform > benzene > toluene, for FY3 materials (can be seen Table 1). The interaction of produced FY3 thin films with VOCs molecules can be explained by physical properties of organic vapors such as molecular weight and molar volume. The molecular weight of organic vapors is given as chloroform (119.38 g mol^{-1}) > toluene (92.14 g mol^{-1}) > benzene (78.11 g mol^{-1}). A larger molecular weight of vapor leads to higher sensitivity, which is in good agreement with the previous findings in the literature [28]. It is reasonable to assume that if the number of adsorbed molecules on an adsorbent is limited and identical for various adsorbents, a greater molar mass of adsorbent would certainly lead to a larger change of response [27]. However, the sensitivity of FY3 LB film sensor against benzene vapor larger than toluene vapor. This can be explained in terms of molar volume of organic vapors and the molar volume of benzene (86.36 cm^3 mol^{-1}) is smaller than the toluene (107.00 cm^3 mol^{-1}). While benzene molecule can easily penetrate into FY3 LB films, the diffusion of toluene molecules into the same LB films is slower.
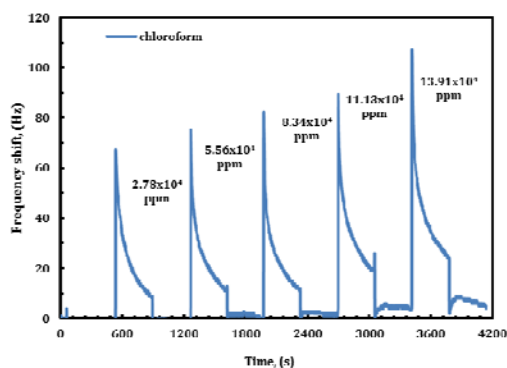

Fig. 7. The response of FY3 LB sensor from 2.98 x 10^4 to 14.94 x 10^4 ppm of chloroform vapors

Table 1. Sensitivity of the FY3-coated QCM sensor to different chemical vapors.

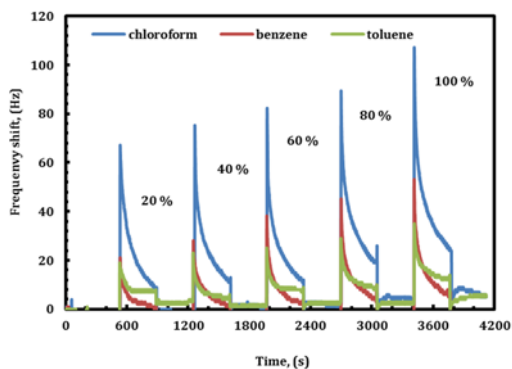| Organic Vapors	Sensitivity (Hz/ppm)x10^{-4}	Detection Limit (ppm)x10^4
Chloroform	3.62	0.83
Benzene	3.22	0.93
Toluene	1.60	1.88

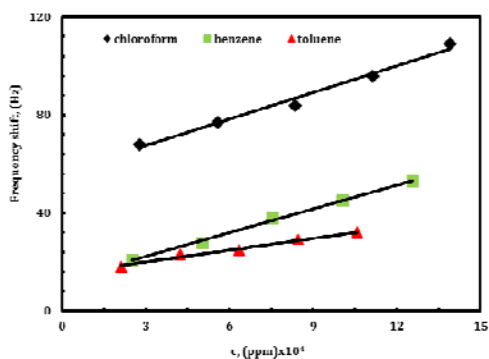Fig. 8. The response of FY3 LB sensor to different concentrations

Fig. 9. Frequency shifts versus concentrations of organic vapors

4. Conclusions

In this study, the LB thin film characterization and vapor sensing properties of 1,7-dibromo- N,N'-(bicyclohexyl)-3,4:9,10- perylendiimide (FY3) materials were investigated using UV-vis spectroscopy and QCM techniques. A plot of UV-vis absorbance value at 495 nm as a function of number of layers indicated a linear relationship. Similar linear relationship was obtained for resonant frequencies versus number of layer using QCM measurement. The typical Δf per layer is obtained as 50.15 Hz / layer and the deposited mass onto quartz crystal is calculated as 399.36 ng / layer (1.50 ng mm^{-2}). FY3 LB film was exposed to chloroform, benzene and toluene vapors. The kinetic measurement of this LB film shows fast, reproducible and reversible response to all vapors. The sensitivies of the FY3 LB film sensor against organic vapors were obtained between 3.62 x 10^{-4} and 1.60 x 10^{-4} Hz ppm^{-1}. Detection limits were found to be between 0.83 x 10^4 and 1.88 x 10^4 ppm for various organic vapors. It can be proposed that the sensing element deposited onto quartz crystal substrate has good sensitivity and selectivity to chloroform vapor. As a result, this FY3 material can be used as a sensing material and may find potential applications in the development of room temperature organic vapor sensing devices.

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