



## Thin film characterization and vapor sensing properties of a novel perylenediimide material

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### ABSTRACT

A novel *N,N*-(glycine tert-butylester)-3,4,9,10-perylenediimide was chosen for the study of Langmuir–Blodgett (LB) thin film characterization and the sensing properties against selected volatile organic vapors. Different number of LB film layer was deposited onto a glass and quartz crystal substrate. The thin film fabrication process was monitored with UV–vis and quartz crystal microbalance (QCM) measurement techniques. The results indicated that absorbance increased linearly with the number of the layers on film. A similar linear relationship between frequency shift and number of the layers was observed by the QCM measurement. It can be concluded that high quality and uniform LB films were produced by using this novel perylenediimide material. Chloroform, toluene, benzene, ethyl alcohol and isopropyl alcohol vapors were selected to test this material's applicability in room temperature as a vapor sensor. This novel material showed a fast, large and reproducible response to chloroform and isopropyl alcohol vapor.

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### 1. Introduction

Perylene and its derivatives are among the most extensively investigated chromospheres in dye chemistry due to their high absorption coefficient for visible light as well as their high chemical and thermal stability with a high quantum yield [1–3]. They have found many potential applications in many areas such as photochemistry [4], photophysics [5], organic solar cells [6–8], photovoltaic devices [9,10], dye lasers [3,11,12], molecular switches and wires [13–15], light-harvesting arrays [16,17], photoreactive thin films [18,19], organic light emitting diodes [20–22], photosensitizers [23], thin films [24] and organic nanodevices [25]. Another possible application of perylenediimide molecule is use as sensing layers of gas sensors, which are based on a change in the conductivity [26], absorbance [27], or fluorescence [28] of thin films under the influence of gas molecules adsorbed on film surface or diffusing into the films. A combination of a sexithiophene and a perylenediimide was used to prepare a semiconductor-doped insulator (MSDI) heterojunction designed with only phthalocyanines as active materials for the detection of ozone and ammonia molecules. This study enlarges the potentialities of the MSDIs and opens the way to their promising development in the field of a new transducer for gas sensing [29]. As a novel vapor detecting material against VOCs, perylene bisimide-bridged bis-(permethyl-*b*-cyclodextrins) mate-

rial was selected to investigate  $\pi$ – $\pi$  stacking interactions in organic and aqueous solutions by UV–vis and fluorescence spectroscopy. The results of this work summarized that fluorescent solids can be used as sensors for gases or fluids and can probe several kinds of VOCs. They exhibit high sensitivity to organic amines [30]. 3,4,9,10-Perylenetetracarboxylicdiimide derivative was another candidate material for fluorescent gas sensors [31]. Thin film of polymethylmethacrylate (PMMA) doped with perylene provides selective and easily prepared optical sensor films for NO<sub>2</sub> gas with suitable response times [32].

To our knowledge, there is no work in the literature, investigating volatile organic vapor (VOCs) sensing properties of perylene molecule based on mass change using Quartz Crystal Microbalance (QCM) measurement system during the influence of gas molecules adsorbed on the thin film surface or diffusing into the thin film. The small number of studies on some perylene molecules only investigates VOC sensing properties for use in electrical measurement systems [26,33] and fluorescence spectroscopy [30,34]. A supramolecular assembly fabricated from perylene bisimides and cyclodextrin conjugates was used as a solid-state fluorescence sensing device for several VOCs. In this study, perylene bisimides act as a fluorescence probe due to their strong fluorescence, photochemical stability and exhibited fluorescence quenching to several saturated vapors such as organic amines and organic solvents [30]. A self-assembly of an asymmetrical, amphiphilic perylene bisimide (PBI) derivative-cyclodextrin conjugate exhibits a solid-state emission, which can act as fluorescence sensory material for vapor detection. The results indicate that a better sen-

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sitivity with a higher selectivity for organic amines that strengthen  $\pi$ -stacking of PBI backbones which leads effectively to improving the probing property of PBI-cyclodextrin conjugates [28]. Other fluorescence sensory material namely, *N*-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide, was fabricated for vapor detection of organic amines with high sensitivity, selectivity, and photostability [34]. To study the diffusion effect using electrical measurement methods, thin films of crystalline *N,N'*-dimethylperylene-3,4,9,10-biscarboximide or amorphous 1,6,7,12-tetrachloro-*N,N'*-dimethylperylene-3,4,9,10-biscarboximide were prepared by physical vapor deposition and characterized by conductivity and field effect measurements under increasing partial pressure of oxygen, ethanol, acetone, or *n*-butane. Changes in the conductivity of the films were observed and field effect measurements indicated a difference between the charge carrier mobility and the charge carrier concentration due to the diffusion effect of vapor molecules [26]. Thin films of several new perylene materials such as polymethylmethacrylate doped with perylene [32], *N,N'*-bis(2-phosphonoethyl)-3,4,9,10-perylenetetracarboxylicdiimide [31], *N,N'*-dioctyl-3,4,9,10-perylenetetracarboxylicdiimides [35] and oligothiophene/bisphthalocyanine were extensively studied as candidate materials in the field of gas sensing applications. Perylene derivatives have a very compatible molecular structure for the design of thin films and suitable for the fabrication of Langmuir–Blodgett (LB) thin films in the nanoscale [36,37]. LB technique can be applied extensively in designing functional molecular devices such as gas or organic vapor sensors with highly oriented structure, controllable thickness and the intramolecular interactions inside the layers as well as on interactions between organic layers and gas or vapor molecules [38,39].

In the present work, a novel *N,N'*-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) material is selected to investigate thin LB film characterization and sensing properties against organic vapors such as chloroform (CHCl<sub>3</sub>), toluene (C<sub>7</sub>H<sub>8</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), ethyl alcohol (CH<sub>3</sub>CH<sub>2</sub>OH) and isopropyl alcohol (CH<sub>3</sub>CHOHCH<sub>3</sub>). Our results showed that the FY1 monolayer has a very uniform arrangement at the air-water interface and they are transferred as LB layers onto the QCM crystal and glass substrates with a high transfer ratio. The 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. This novel material showed very promising results in the vapor sensor application area with a fast, large and reproducible response to chloroform and isopropyl alcohol vapor.

## 2. Experiment details

Fig. 1 shows the chemical structure of a novel *N,N'*-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) molecule. The amine used was tert-butylester of glycine because structural modification of the groups attached to the imide nitrogen improves solubility and aggregation characteristics. A mixture of 3,4,9,10-perylenetetracarboxylic acid dianhydride and glycine tert-butylester hydrochloride in 5 mL H<sub>2</sub>O, 5 mL *n*-butanol and 1 mL triethylamine was stirred for 48 h at 85 °C. This dye was purified by silica gel column chromatography. After drying the pure material, a sample was prepared in CDCl<sub>3</sub> for <sup>1</sup>H-<sup>13</sup>C NMR analysis.

- (1) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm], 1.45 (s, 18H, -C(=O)O-C), 4.75 (s, 4H, N-CH<sub>2</sub>), 8.23 (d, *J*=8.06, 4H, CH-arom), 8.38 (d, *J*=7.93, 4H, CH-arom).
- (2) <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm], 28.5, 30.1, 110.8, 114.5, 116.2, 120.6, 123.6, 126.9, 132.1.

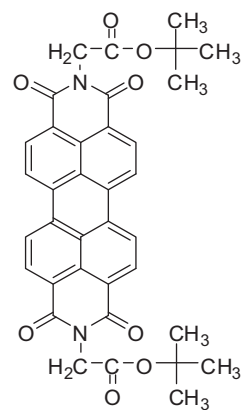


Fig. 1. Chemical structure of FY1 molecule.

Fully computer-controlled NIMA 622 LB trough with an area of 1200 cm<sup>2</sup> was used to investigate the monolayer at the air-water interface and the LB film transfer onto solid substrates. Solutions of FY1 in chloroform with a concentration of ~0.1 mg ml<sup>-1</sup> were spread onto ultra pure water subphase to investigate the behavior of FY1 molecule at air-water interface by taking surface pressure (*Π*) as a function of surface area (A) called as *Π*-A isotherm graph. The pH value of the subphase is nominally maintained at 6. A time period of 15 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. The temperature of the water subphase was controlled using Lauda Ecoline RE 204 model temperature control unit and all experimental data were taken at room temperature. Isotherm graphs were repeated three times and the results were found to be reproducible.

After taking the *Π*-A isotherm graphs, the floating monolayer at the water surface was found to be stable at the surface pressure of 22.5 mN m<sup>-1</sup> for a period of 15 min and this surface pressure value is selected for LB film deposition on glass substrates and on quartz crystals for UV-vis and QCM measurements, respectively. The deposition mode for LB film was of the Y-type and vertical dipping procedure was performed at the selected surface pressure with a speed of 25 mm min<sup>-1</sup> for both the down and up strokes. LB film samples were left to dry after each up stroke. Different numbers of monolayer were deposited on these substrates under the same surface pressure.

The UV-vis spectra of LB film were recorded in the visible spectral region from 400 nm to 600 nm using an Ocean Optics UV-vis light source (DH-2000-BAL Deuterium Tungsten light source) and spectrometer (USB4000) in absorbance mode. FY1 material in chloroform was measured in quartz cuvettes. After the deposition of LB film multilayer onto glass substrates, UV-vis spectra were recorded as a function of number of layers.

For QCM studies, FY1 material was deposited onto a thinly cut wafer of raw quartz sandwiched between two gold electrodes in an overlapping keyhole design. After each deposition cycle, the LB film sample was dried and the mass change was monitored using a home-made computer controlled QCM measurement system. Dedicated software allows the on-line recording of the changes of the quartz resonance frequency. All measurements were taken at room temperature using an in-house designed oscillating circuit and standard quartz crystals with a nominal resonance frequency of 7 MHz. The quartz crystal was inserted into the electronic control unit and the frequency of oscillation was monitored as a function of time using a computer. Values of frequency changes, which indicate the degree of response, are measured with an accuracy of 1 Hz when the organic vapor is present.

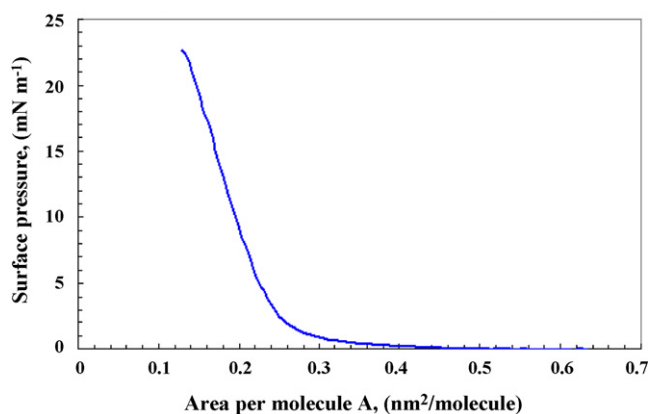


Fig. 2. Isotherm graph of FY1 monolayer.

### 3. Results and discussion

#### 3.1. Isotherm and transfer ratio

The surface pressure versus surface area ( $\Pi$ - $A$  graph) is an important graph to understand the characteristic surface behavior of a floating monolayer on the water surface. The area per molecule for a floating monolayer can be calculated using this following relation:

$$a_m = \left( \frac{AM_\omega}{cN_A V} \right) \quad (1)$$

where  $A$  is the area of the water surface enclosed by the trough barriers,  $M_\omega$  is the molecular weight,  $c$  is the concentration of the spreading solution,  $N_A$  is the Avagadro's number and  $V$  is the volume of solution spread over the water surface.  $\Pi$ - $A$  graph obtained from the floating monolayer on the water subphase is given in Fig. 2. The surface pressure starts rising at an area around  $0.4 \text{ nm}^2$  until the surface pressure reaches to  $23 \text{ mN m}^{-1}$ . The limiting area per molecule obtained by extrapolating the slope of low compressibility to zero pressure indicates  $0.25 \text{ nm}^2$ . Menikh and his group studied the isotherm graph of  $N,N'$ -bis(decamethylcarboxylic)-3,4,9,10-perylene-bis(dicarboxyimide) molecule and a similar  $\Pi$ - $A$  isotherm has been observed with the limiting area per molecule which was found to be  $0.4 \text{ nm}^2$  using the extrapolating method [40].

$\Pi$ - $A$  isotherm measurements were repeated several times using identical and differing volumes of the solution and the results demonstrated good stability and reproducibility of the monolayers at the water surface. The floating monolayer at water surface was found to be stable at a surface pressure of  $22.5 \text{ mN m}^{-1}$  that was selected for LB film deposition procedure. Similar surface pressure value ( $25 \text{ mN m}^{-1}$ ) is chosen for perylenetetra-carboxylicdiimide molecule [37].

The transfer ratio (TR) for an LB deposition is also an important parameter to monitor the deposition process and it is defined as the ratio of the area of the LB film removed from the water surface to the area of the substrate moved through the air-monolayer-water surface.

$$\text{TR} = \frac{A_1}{A_2} \quad (2)$$

where  $A_1$  is the decrease in the area occupied by the monolayer on the water surface and  $A_2$  is the coated area of the substrate. The TR was calculated between 0.90 and 1.00 for Y-type LB film. The transfer ratio for  $N,N'$ -bis(decamethylcarboxylic)-3,4,9,10-perylene-bis(dicarboxyimide) molecule was found to be 0.98 [40]. Our results can be concluded that stable and reproducible

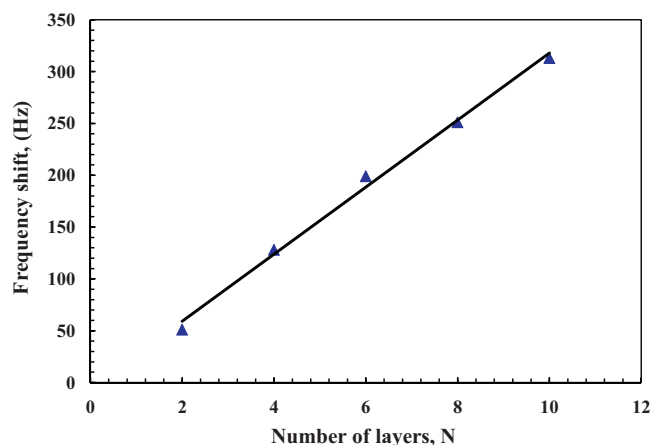


Fig. 3. The transfer graph of FY1 LB film on the quartz crystal.

monolayers of FY1 were formed on the water surface, and that a uniform LB deposition successfully fabricated onto solid substrates.

#### 3.2. QCM measurements

LB film multilayers were produced on a quartz crystal substrate that consists of thin quartz disc sandwiched between a pair of gold electrodes. Due to the piezoelectric properties of quartz crystal, it is possible to investigate the relationship between the resonant frequency change and mass change. For an LB film,  $\Delta f$  must be related directly to mass of the bilayer given by:

$$\Delta f = -\frac{2f_0^2 \Delta m}{\rho_q^{1/2} \mu_q^{1/2} A} N \quad (3)$$

where  $N$  is the number of deposited layers and  $\Delta m$  is the deposited mass per unit area per layer (g).  $\Delta f$  is the frequency change (Hz),  $f_0$  is the resonant frequency of the crystal (Hz),  $A$  is the electrode active area ( $\text{cm}^2$ ),  $\rho_q$  is the density of quartz ( $2.648 \text{ g cm}^{-3}$ ),  $\mu_q$  is the shear modulus of quartz ( $2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$ ).

Fig. 3 shows a plot of the change in the resonant frequency against number of layers for FY1 LB film. It is clear that a systematic change in the frequency is observed with the increase in the number of monolayers. This linear change between the deposited mass and the number of layers confirms the uniform transfer process of the LB film and the process was shown to be highly reproducible. The gradient of this graph shows the typical frequency shift,  $\Delta f$ , is  $32.4 \text{ Hz}$  per bilayer. The mass deposited onto quartz crystal per bilayer can be calculated as  $74.5 \text{ ng}$  for FY1 LB film using Eq. (3).

#### 3.3. UV-vis measurements

UV-vis absorbance spectra of FY1 molecule in chloroform solution with a concentration of  $\sim 0.1 \text{ mg ml}^{-1}$  is shown at Fig. 4. The solution spectrum exhibits three absorption peaks at 455, 487 and  $524 \text{ nm}$ . They are identical to a progression of  $\pi$ - $\pi^*$  transitions of perylene ring and are in good agreement with the literature values taken with other perylene materials [41]. Perylenediimides exhibit strong absorption of light in the wavelength range  $450$ – $550 \text{ nm}$  and near unity quantum yield of fluorescence between  $540$  and  $620 \text{ nm}$  [3]. 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 [42]. A UV-vis spectra

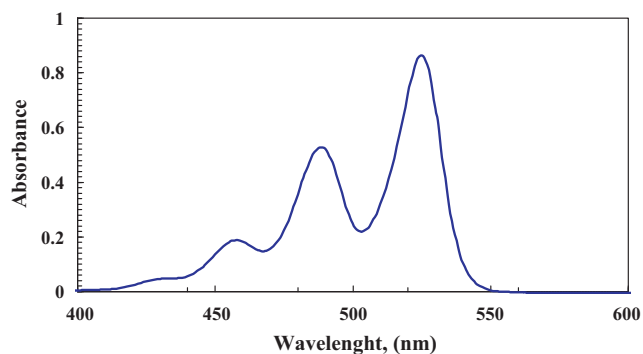


Fig. 4. UV-vis spectra of FY1 in a chloroform solution. (Peaks are 455, 487 and 524 nm.)

and fluorescence emission of a novel perylene diimide (PDI) which contains a bay region hydroxyl function was studied to monitor the sensing behavior as a pH-sensitive dye. In a chloroform solution, this novel PDI material has two absorption peaks at 520 and 555 nm with a shoulder at 480 nm [43]. Another UV-vis and fluorescence work was carried out in a chloroform solution using an asymmetrical perylene diimide 3, *N*-(4-methoxyphenyl)-*N*′-(4-nitrophenyl)-perylene-3,4,9,10-tetracarboxylic diimide material. The concentration-dependent of UV-vis absorption spectra in chloroform exhibited three absorption peaks at 528, 491 and 460 nm due to typical monomeric  $\pi$ - $\pi$  transition band. However with high concentration rates (above  $10^{-6}$  mol/L), an additional broad peak appeared at longer wavelength (577 nm) corresponds to the absorption of the aggregates composed of  $\pi$ - $\pi$  stacking species [44].

In our present work, UV-vis results were also used to monitor the deposition process of LB thin film multilayers on quartz substrates by taking intensity of the absorption peaks as a function of number of layers given in Fig. 5. Intensity of the absorption peaks increases when the number of layers increases. In the spectrum of the LB films deposited from the water surface, obvious band broadening was observed. This could be ascribed to the field effects of the closely compacted molecular assembly [37]. The main absorption bands in chloroform solution appeared at 455, 487 and 524 nm. UV-vis spectra of FY1 LB films exhibit slightly (about 9 nm) red-shifted absorption bands compared to the spectrum of the chloroform solution. This has been reported previously for LB films of other PDIs [28,37,45,46]. The shift in the absorption

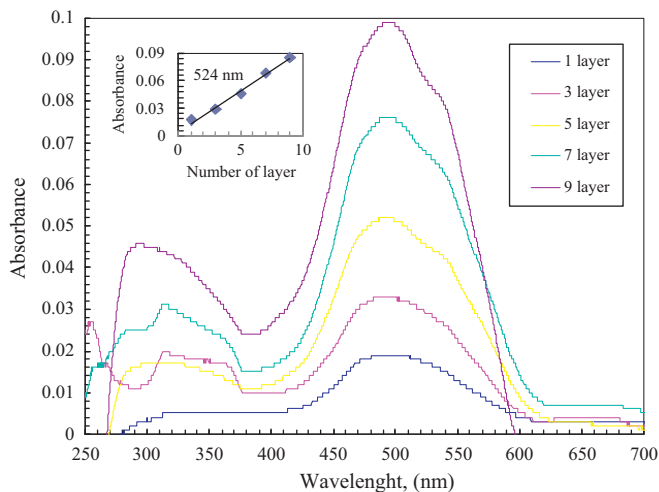


Fig. 5. UV-vis spectra of FY1 film. (The inset: absorbance as a function of number of layers at 524 nm.)

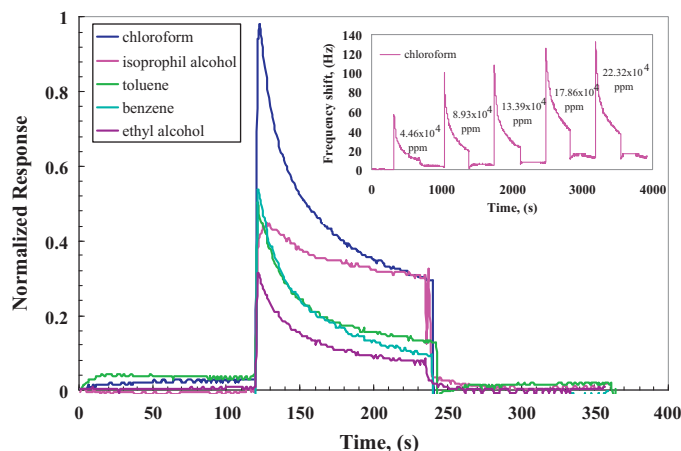


Fig. 6. The frequency change of FY1 LB film against organic vapors.

band of the LB film may be the result of some kind of molecular aggregation which takes place during film formation. This shift has been attributed to two possible reasons such as an edge-to-edge aggregation of the PDI molecules in the monolayer film and the conformational change of the PDI macrocycle from nonplanar structures in solution to planar structures in solid films [37]. When comparing the limiting molecular area of the PDI monolayer on the water surface, it is unlikely that the PDIs formed edge-to-edge aggregation within the monolayer film. It is more reasonable to attribute the red shift of the main absorption bands to a greater  $\pi$ -electron delocalization in the film than in solution because of the more planar conformation of the macrocycle in the film [37]. Unlike two bands are observed in the spectra of the films instead of three in the solution spectrum. Similar results are reported using novel fluorinated perylene diimide and *N,N*′-diperfluorophenyl-3, 4, 9, 10-perylenetetracarboxylic diimide. The fine structure of the absorptions of solution disappeared and the peaks became broader due to the molecular absorptions, implying that the  $\pi$ - $\pi^*$  coupling did not exist [41], or may be caused by the aggregation of perylene moiety [47].

The linear relationship between the number of layers and the absorbance at 500 and 524 nm of FY1 LB film was obtained in the inset of Fig. 5. The fact suggests that the monolayer is transferred uniformly from water surface onto the substrate and the microscopic environment of FY1 molecule remains unchanged throughout the layers.

#### 3.4. Sensing properties of FY1 LB film

There is not much information in the literature on the study of mass change sensing application of perylene-based materials as a gas sensing application using QCM technique. In order to study the potential application of FY1 LB film in the field of VOCs sensing, the kinetic response of the LB sample to the chloroform, benzene, toluene, ethyl alcohol and isopropyl alcohol vapors was recorded by measuring the frequency changes as a function of time at room temperature. The LB film sample was periodically exposed to the organic vapor for 2 min, followed by the injection of dry air for a further 2 min period. Values of  $\Delta f$ , which indicate the degree of response, are measured with an accuracy of 1% Hz. Fig. 6 shows the kinetic response of the FY1 LB film to all vapors. This LB film shows a response to all vapors with a fast, reproducible and reversible response after flushing the gas cell with fresh air. LB film sample used FY1 material is found to be more sensitive to chloroform and isopropyl alcohol vapors than other organic vapors. As soon as dry air was injected to the gas cell, LB sample was found to

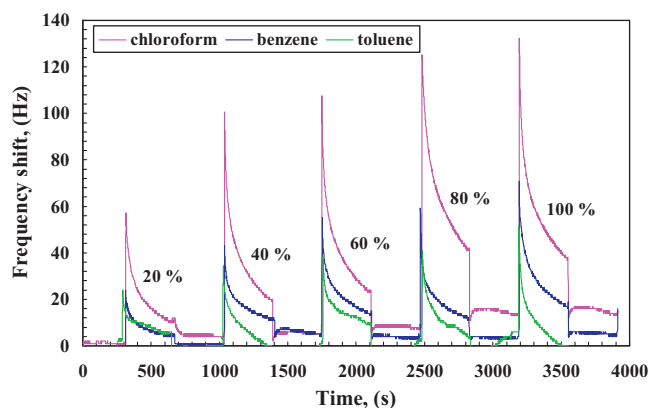


Fig. 7. The response of FY1 LB sensor to different concentrations.

recover almost fully. The response of the LB film in the form of QCM response to saturated chloroform exposures is larger than the other vapors with recovery times in the order of a few seconds (3 s for response and 4 s for recovery times) when the gas cell is flushed with dry air. All the response measurements of the FY1 LB film to organic vapors were run three times, and the results showed that the sensor responses were reproducible. The reproducible response for chloroform with different concentration value diluted by air is given the inset in Fig. 6. The frequency shift increases when the concentration of chloroform increased. This film also yields a relative stable repeatability, a good reproducibility and almost uniform changes in frequency.

In general, the mechanism of gas permeation into the sensing material can be considered by three "solution-diffusion" steps, i.e., adsorption, diffusion, and desorption process. The frequency changes sharply when LB film is introduced with organic vapors, which results from surface adsorption effect [48]. Then, the frequency increases slowly because of bulk diffusion effect between sensitive FY1 LB film and vapor. This interaction process is called a dynamic process where adsorption and desorption processes occur simultaneously. When the number of adsorbed vapor molecules is equal to the number of desorbed vapor molecules, the frequency reaches a stable value. After flushing the air, a rapid increase of frequency will occur due to desorption of vapor which is a surface and bulk effect. To compare the sensitivity, frequency shifts of the organic vapors is plotted in Fig. 7. Our results showed that chloroform has the largest frequency shifts compared to the others. This can be explained taking into account molecular weights. A larger molecular weight of vapor leads to higher sensitivity, which is in good agreement with the previous findings in the literature [49]. 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 frequency shift [48]. When we compare the response of FY1 against benzene and toluene vapors, toluene response is slightly higher than benzene because of the molecular weight of toluene is higher than benzene vapor. Similar analysis can be given for alcohols (isopropyl alcohol and ethyl alcohol) with the same molecular weight explanation. Fig. 7 gives the typical frequency-response of the FY1 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. Furthermore, the FY1 LB film exhibits a rapid and fast reversible response. Fig. 8 shows that the correlation between the frequency shift ( $\Delta f$ ) of the FY1 LB film and gas concentration. It was found that with the enhancement of gas concentration, the frequency shift increases and has almost linear response to gas concentration for chloroform, benzene and toluene.

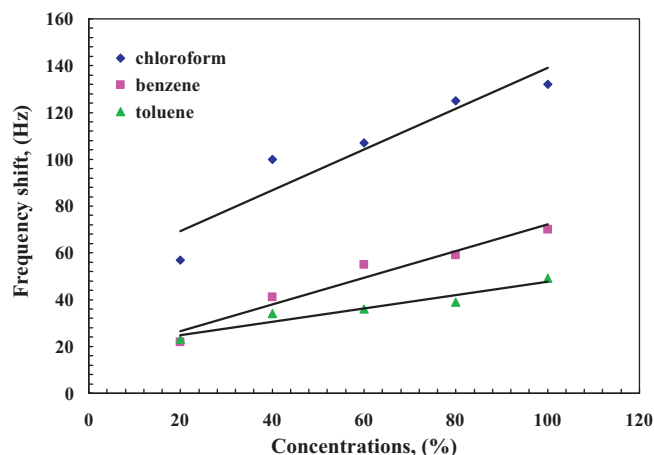


Fig. 8. Frequency shifts versus concentrations of organic vapors.

**Table 1**  
Sensitivity of the FY1-coated QCM sensor to different chemical vapors.

Organic vapors	Sensitivity (Hz/ppm) $\times 10^{-4}$	Detection limit (ppm) $\times 10^4$
Chloroform	3.91	1.53
Benzene	3.50	1.71
Toluene	3.22	1.86

The limit of detection (LOD) of the FY1 LB film sensor was calculated by the measured sensor sensitivity (Hz/ppm). LOD was defined by [48]:

$$\text{LOD} = \frac{3\sigma}{S} \quad (4)$$

where  $\sigma$  is the noise level of the fabricated QCM sensor;  $S$  is the sensitivity to a specific analyte of the sensor. In this study, the resonance frequency was recorded in air for use as the absolute frequency of the QCM system, and the frequency response was stable within  $\pm 2$  Hz over a period of 30–45 min. Therefore the frequency noise was estimated at 2 Hz. The sensitivity and detection performance of the fabricated QCM sensor to several volatile organic vapors is given in Table 1 that FY1-coated QCM sensor displayed sensitivity with detection limits of  $\sim 1.53$ – $1.86 \times 10^4$  ppm for various organic vapors at room temperature.

#### 4. Conclusion

A novel *N,N'*-(glycine *t*-butylester)-3,4,9,10-perylene diimide (FY1) is successfully deposited onto glass and quartz crystal substrates by Langmuir–Blodgett thin film deposition technique. A value of the area per molecule is found to be  $2.25 \text{ nm}^2$  using isotherm graph taken at the water surface and this floating monolayer is successfully deposited onto the solid substrates with a high transfer ratio between 0.90 and 1.00. UV–vis and QCM measurements indicate that highly ordered and uniform LB film is produced using FY1 material. This material gives a large response to chloroform and isopropyl alcohol vapors than other vapors. The responses in terms of frequency change to the exposure of chloroform and isopropyl alcohol vapors are fast, large and reversible. The FY1 LB film may find potential applications in the development of room temperature vapor sensors for VOCs. Therefore, gas sensors based on FY1 are very promising for environmental and industrial applications. To further this work, we will study the sorption processes during sensor application and influence of other gases in the ambient air.

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