



# Characterization and organic vapor sensing properties of Langmuir–Blodgett film using a new three oxygen-linked phthalocyanine incorporating lutetium

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## ABSTRACT

In the present article we report about the Langmuir–Blodgett thin film characterization and organic vapor sensing properties of LB film properties of three oxygen-linked phthalocyanines incorporating lutetium (Pc<sub>2</sub>Lu). UV–visible spectroscopy and quartz crystal microbalance are used for the characterization of Pc<sub>2</sub>Lu material. Our results show that high quality and uniform LB films can be prepared with the transfer ratio ~0.95 and this material is found more sensitive to chloroform and isopropyl alcohol vapors than other organic vapors used in this work. The response, in terms of frequency change to the exposure of these vapors, is fast, large and reversible.

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## 1. Introduction

The detection of volatile organic compounds (VOCs) is a very important task due to stringent environmental standards and regulations on VOCs in many countries of the world and their natural toxicity is dangerous for the environmental and human being. These compounds are highly dangerous and can cause many disease such as acute, chronic or long-term effects such as affecting the nose, throat and lungs that asthma-like reactions, eye irritation and cancer. Phthalocyanines (Pc) have attracted considerable attention as a sensitive material because of their electrical, optical, redox properties, a good thermal and chemical stability and are suitable materials to form as a thin film compatible with microelectronic devices [1–3]. In the last decade, the possible application of Pc thin films as sensors for atmospheric gaseous pollutants has been extensively studied [4–6]. Unfortunately, the response of the thin films of Pc towards VOCs has not been so extensively studied [7]. Basova et al. [6] Pc material is used as a sensing element against chloroform and benzene vapors. The results indicated that the formation of hydrogen bonds with alkyl chains of the substituents occurred through the interaction with saturated C–C bonds chloroform and

the sensor response to benzene is believed to be due to their  $\pi$ – $\pi$  interaction with the conjugated Pc ring. The introduction of different central metal ions into Pc compound turns out to be powerful means of modifying the chemical and physical properties of phthalocyanines [8]. The bisphthalocyanine of lutetium (LuPc<sub>2</sub>) is an attractive material for the detection of VOCs due to its high sensitivity, fast response times, repeatability and the variety of responses it produces and the sensitive layers was used for several months without significant loses in sensitivity [7]. Pc<sub>2</sub>Lu with a high concentration of intrinsic charge carriers and a low-thermal activation energy of conduction is used as a sensitive element of a gas sensor using HCl, Cl<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub> and SO<sub>2</sub> [3].

In the present article, a multifunctional compound having a sandwich structure with a new type of unsymmetrical and trimeric trilutetium hexaphthalocyanine involving oxygen bridged three double-deckers (Pc<sub>2</sub>Lu) material is selected to form as a sensing layer onto a quartz crystal using Langmuir–Blodgett Thin Film Technique. UV–visible spectroscopy and quartz crystal microbalance (QCM) measurement system are employed to monitor the thin film deposition process. QCM measurement system is also used to detect the organic vapor such as chloroform, toluene, benzene, ethyl alcohol and isopropyl alcohol.

## 2. Experimental details

A NIMA 622 alternate LB trough was used to investigate the behaviour of the molecules at the air–water surface and fabricate

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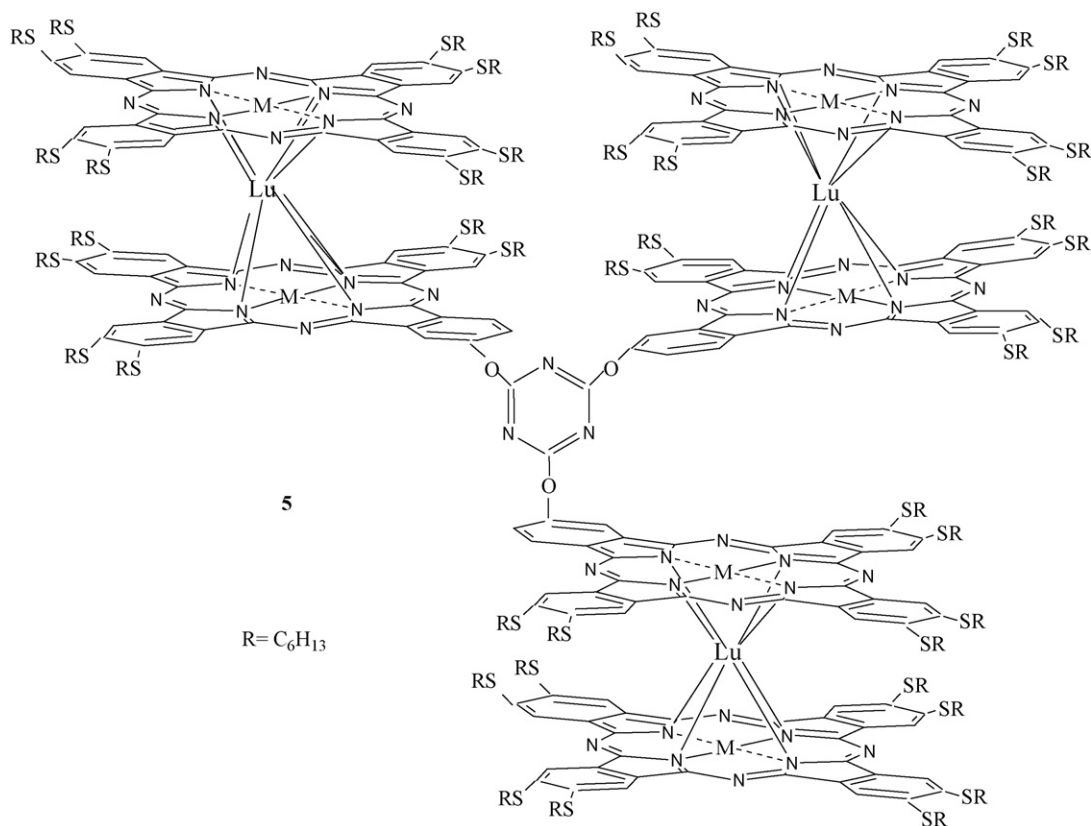


Fig. 1. Chemical structure of material.

LB film multilayers onto glass and quartz crystal substrates.  $\text{Pc}_2\text{Lu}$  material dissolved in chloroform with concentration of  $\sim 0.3 \text{ mg ml}^{-1}$ , which was spread onto ultra pure water subphase at pH 6. A time period of 15 min was allowed for the solvent evaporate before the area enclosed by the barriers was reduced. The isotherm ( $\pi$ -A) graph of  $\text{Pc}_2\text{Lu}$  molecule was recorded as a function of surface area using the compression speed of barriers at a value  $1000 \text{ mm min}^{-1}$ . 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. Monolayer of  $\text{Pc}_2\text{Lu}$  material at the water surface was found to be stable and surface pressure of  $22.5 \text{ mN m}^{-1}$  was selected for LB film deposition on the solid substrates such as a quartz for UV-visible and a quartz crystal for QCM measurements. Y-type LB deposition mode and a vertical dipping procedure was performed at the selected surface pressure with a speed of  $25 \text{ mm min}^{-1}$  for both the down and up strokes. LB film sample was dried after each up stroke. The UV-visible spectra of LB film were recorded in the ultraviolet and visible spectral region from 250 nm to 800 nm using a VARIAN CARY 1E UV-visible spectrophotometer in the absorbance mode. A thinly cut wafer of raw quartz sandwiched between two electrodes in an overlapping keyhole design was used for the QCM measurement. QCM measurements were performed at room temperature using an in-house designed oscillating circuit and standard quartz crystal with a nominal resonance frequency of 4 MHz. The frequency was measured with a MOTECH FG-513 model function generator and TEKTRONIX TDS 210 model digital oscilloscope. The QCM technique can be easily applied to monitor the kinetic response of Pcs LB films against organic vapors using a special gas cell. The variation of the frequency changes was monitored as a function of time when the sample was periodically exposed to the organic vapors

for at least 2 min and was allowed to recover after injection of dry air.

### 3. Results and discussion

Fig. 1 shows the chemical structure of three oxygen-linked Pcs incorporating lutetium ions and the details of the synthesis and characterization of this material can be found in the literature [8]. Surface pressure–area ( $\Pi$ -A) graph of  $\text{Pc}_2\text{Lu}$  at the room temperature is shown in Fig. 2. The surface pressure increases with decreasing the surface area. The area per molecule in the solid phase obtained by a linear extrapolation of the isotherm to the area axis

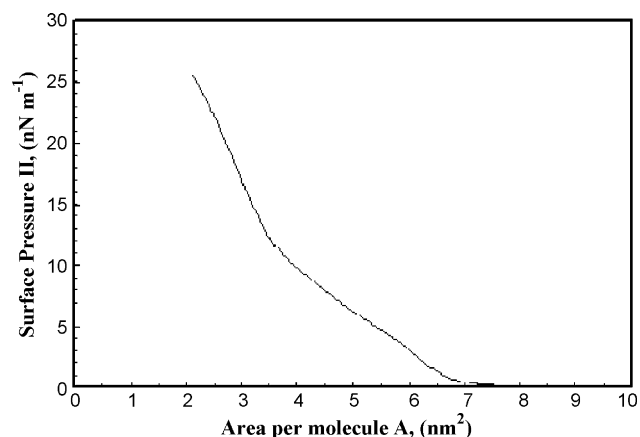


Fig. 2. Isotherm graph of  $\text{Pc}_2\text{Lu}$ .

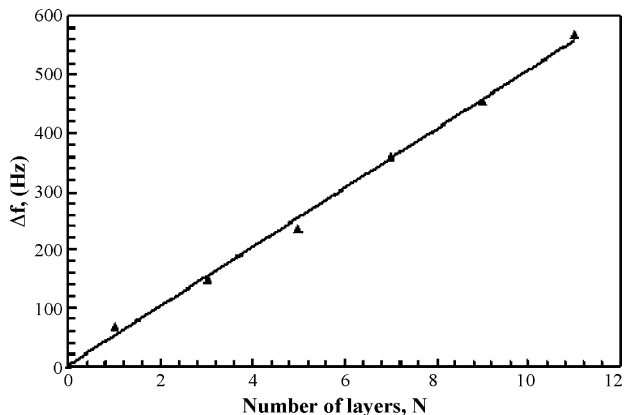


Fig. 3. The transfer of Pc<sub>2</sub>Lu LB film on the quartz crystal.

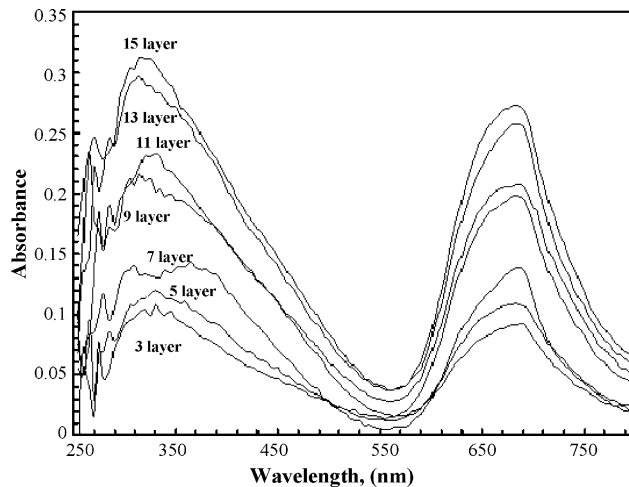


Fig. 5. UV-visible spectra of Pc<sub>2</sub>Lu film (peak values for Pc<sub>2</sub>Lu: 317 and 685 nm).

is 4.7 nm<sup>2</sup>. From the analysis of the isotherm, a surface pressure of 22.5 mN m<sup>-1</sup> was chosen for the deposition processes and the transfer ratio was ~0.95 for Y-type LB film. A stable and reproducible monolayer of Pc<sub>2</sub>Lu at the water surface and a uniform LB deposition occurred onto a glass or quartz crystal substrate. Isotherm graph was taken several times using the same experimental conditions and the results were found to be reproducible.

The monitor of the deposition process of the LB film is carried out using QCM system. In LB films, the frequency shift, Δf, must be related with the deposited mass onto the quartz crystal. Δf is given by [9]:

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

where f<sub>0</sub> is the resonant frequency of the crystal (Hz), Δm is the mass change (g), A is the area (cm<sup>2</sup>), ρ<sub>q</sub> is the density of quartz (2.648 g cm<sup>-3</sup>), μ<sub>q</sub> is the shear modulus of quartz (2.947 × 10<sup>11</sup> g cm<sup>-1</sup> s<sup>-2</sup>), N is the number of deposited layers.

Fig. 3 gives the frequency change as a function of frequency for the Pc<sub>2</sub>Lu LB film. This linear change confirms the uniform transfer process of the LB film and indicates the equal mass deposited

for each layer. The typical Δf of this graph is found to be 50.7 Hz per bilayer. The mass deposited onto quartz crystal per bilayer is determined 116 ng using Eq. (1). In our previous paper, Δf was 32.5 Hz per bilayer for ZnPc and 27.5 Hz per bilayer for CuPc LB films, the mass deposited on the quartz crystal per bilayer is estimated as 81 ng for ZnPc and 63 ng for CuPc LB films using s-triazines bearing three oxygen-linked Pcs incorporating Cu and Zn metals [10].

Fig. 4 shows that UV-vis spectra of Pc<sub>2</sub>Lu molecule in the chloroform solution and it exhibits two typical absorption bands of Pc derivatives around 300–400 nm (B band) and 600–700 nm (Q band)[8,10]. The absorption band of Pc<sub>2</sub>Lu at 310 nm has been determined a transition of full level molecular orbital to semi-occupied molecular orbital [11]. Q band for Pc<sub>2</sub>Lu is observed at 650 nm and 700 nm by splitting into a doublet. This band is associated with the π → π\* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the alkyl chain.

Fig. 5 displays the UV-vis spectra of Pc<sub>2</sub>Lu films with different numbers of layers. It can be seen that the intensities of the absorption peaks increased as a function of film thickness. In order to

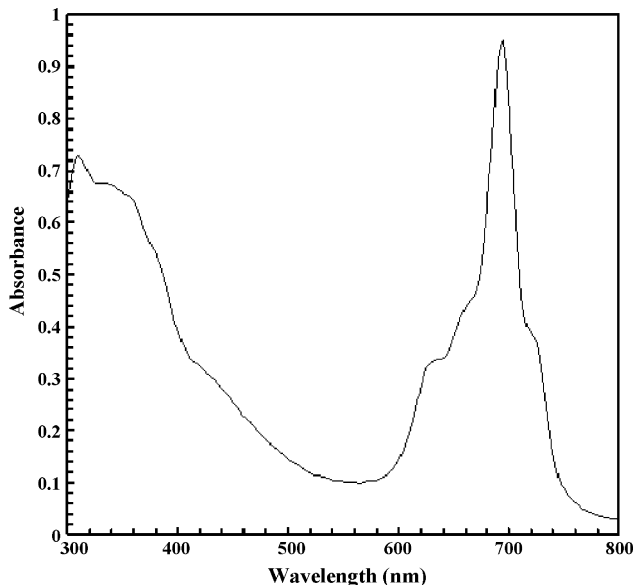


Fig. 4. UV-visible spectra of phtalocyanines in a chloroform solution (peak values for Pc<sub>2</sub>Lu: 315 and 695 nm).

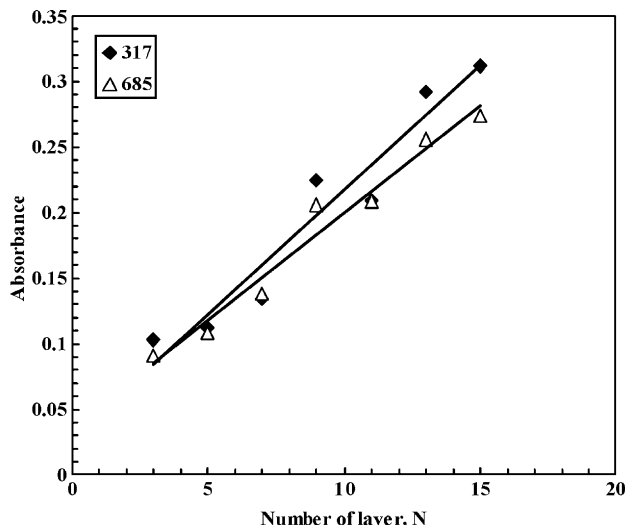


Fig. 6. Dependence of absorbance for Pc<sub>2</sub>Lu film at 317 nm and 685 nm.

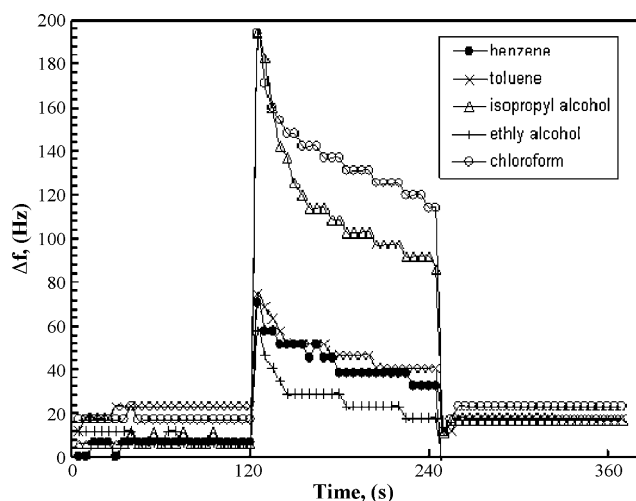


Fig. 7. The frequency change of  $\text{Pc}_2\text{Lu}$  LB film against organic vapors.

monitor the deposition of LB film layer onto the glass substrate, the relationship between the absorbance and film thickness was investigated. A linear dependence of the absorbance on the number of layers confirms the reproducible film deposition onto the glass substrate. Fig. 6 shows a plot of the absorbance of the deposited  $\text{Pc}_2\text{Lu}$  LB films versus the number of LB film layers. These linear relationships confirm that the amount of material deposited is the same in each deposition step.

In order to study the potential application of this  $\text{Pc}_2\text{Lu}$  LB film in the field of vapor sensing properties, the kinetic response of the LB sample to the benzene, toluene, isopropyl alcohol, ethyl alcohol and chloroform vapors was recorded by measuring the frequency changes as a function of time. The  $\text{Pc}_2\text{Lu}$  LB film was periodically exposed to the organic vapor for 2 min, followed by the injection of dry air for a further 2 min period. Fig. 7 shows the kinetic response of  $\text{Pc}_2\text{Lu}$  LB film to the vapors. This LB film has a larger response to chloroform and isopropyl alcohol than other organic vapors and the response to these vapors are fast, reproducible and reversible after flushing the gas cell with fresh air. Similar result is found in our previous work using  $\text{CuPc}$  and  $\text{ZnPc}$  LB films [10].

#### 4. Summary

The LB film and vapor properties of a new  $\text{Pc}_2\text{Lu}$  material are studied in this present article. A value of the area per molecule for  $\text{Pc}_2\text{Lu}$  monolayer at the air–water interface is found to be  $4.7 \text{ nm}^2$  and this monolayer is successfully deposited onto a glass or quartz crystal with a high transfer ratio of  $\sim 0.95$ . This  $\text{Pc}_2\text{Lu}$  LB film is stable and reproducible. QCM result gives a linear relationship between the frequency change and the deposited mass, which confirms that a uniform transfer process occurred during the deposition process. The mass deposited onto quartz crystal is calculated  $116 \text{ ng}$ . UV–vis results supported this uniform deposition of  $\text{Pc}_2\text{Lu}$  molecule with the same amount of material deposited in each deposition step.

The potential application of this  $\text{Pc}_2\text{Lu}$  LB film as a vapor sensing material using benzene, toluene, isopropyl alcohol, ethyl alcohol and chloroform vapors is investigated and the kinetic measurement of this LB film shows fast, reproducible and reversible response to all vapors. A larger response to chloroform and isopropyl alcohol occurred than other organic vapors. Finally, this new  $\text{Pc}_2\text{Lu}$  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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**Rifat Çapan** received MSc degree at Hacettepe University Physics Engineering Department in 1991, Ankara-Turkey and his PhD at the University of Sheffield (UK) in 1998. He established first Langmuir–Blodgett Thin Film Research Group in Turkey. 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. His main interests are pyroelectric heat sensor, gas sensor for environment applications, the electrical and optical properties of organic thin film materials. Dr. Çapan was appointed assistant professor between 1999 and 2002 and associate professor from 2002 to 2007 at University of Balıkesir in Turkey. He became a deputy of head of physics department in 2001 and was the head of physics department between 2003 and 2006. He has been working as a professor and the head of Department at the University of Balıkesir since 2007.

**Özer Bekaroğlu** received BS and MS in chemical engineering from University of İstanbul in 1960, PhD from University of Basel (Switzerland) in 1963 in the field of coordination chemistry. After postdoctoral work at the University of California, Davis between 1964 and 1966, worked at a pharmaceutical company as investment manager 1 year. He became associate professor at the University of İstanbul. Transferred to Technical University of İstanbul and became professor in 1975 until his retirement in 2000. He is still makes research at several universities in Turkey. His research is focused on syntheses and properties of phthalocyanines since 1985.