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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_2Lu). UV–visible spectroscopy and quartz crystal microbalance are used for the characterization of Pc_2Lu 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.

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 π–π 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 phyhalocyanines [8]. The bisphthalocyanine of lutetium ($LuPc_2$) 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_2Lu 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_2, H_2S, NO_2 and SO_2 [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_2Lu) 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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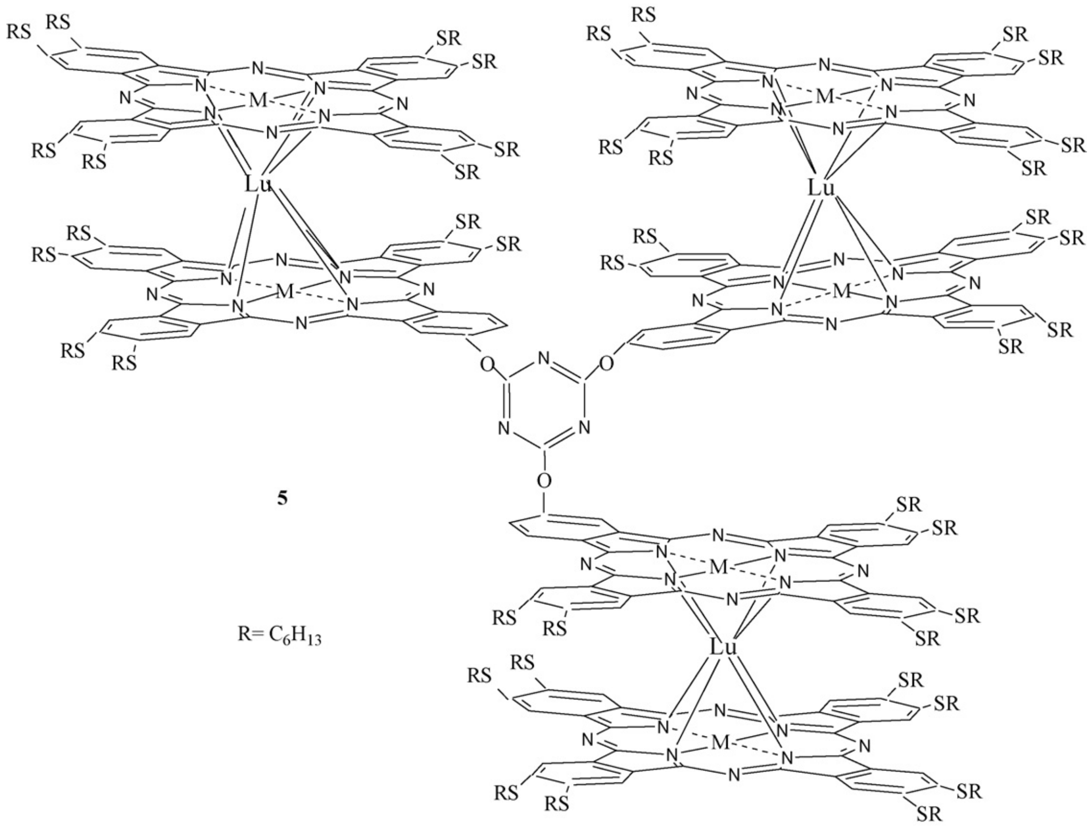

Fig. 1. Chemical structure of material.

LB film multilayers onto glass and quartz crystal substrates. Pc_2Lu material dissolved in chloroform with concentration of ~0.3 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 (π–A) graph of Pc_2Lu molecule was recorded as a function of surface area using the compression speed of barriers at a value 1000 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 Pc_2Lu material at the water surface was found to be stable and surface pressure of 22.5 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 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 TEKTRONİX 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 (Π–A) graph of Pc_2Lu 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

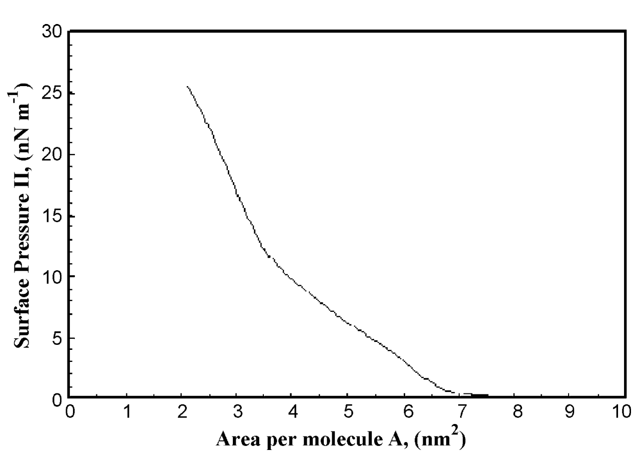

Fig. 2. Isotherm graph of Pc_2Lu.