Synthesis, characterization and chemical sensor properties of a novel Zn(II) phthalocyanine containing 15-membered dioxa-dithia macrocycle moiety

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ABSTRACT

The issue of utilizing organic materials in chemical sensing devices has recently received considerable critical attention. Phthalocyanines (Pcs) and metal phthalocyanines (MPcs) have been identified as promising materials thanks to their outstanding properties reported in this study. A novel zinc(II) phthalocyanine containing four 15-membered dioxa-dithia macrocyclic moieties was synthesized via the reaction of anhydrous Zn(II) acetate and 13,14-dihydro-6H,12H,20H-tribenzo[*f*,*j*,*n*][1,5]dioxa[9,12] dithiacyclopenta-decine-2,3-dicarbonitrile which was prepared from 1,3-di(2-thio-methylphenoxy) propane and 4,5-dichlorophthalonitrile. In order to synthesize and characterize this novel compound, elemental analysis, MS, FT-IR, ^{1}H, ^{13}C NMR, and UV–vis spectral techniques were utilized. To create a Quartz Crystal Microbalance (QCM) sensor, zinc(II) phthalocyanine-based macrocyclic molecules were deposited onto a quartz crystal using the Langmuir-Blodgett (LB) thin film technique. The sensing ability of this chemical sensor was examined by recording the interaction between this novel material as a QCM-sensor and selected chemical vapors such as carbon tetrachloride, chloroform, benzene and toluene. The interaction results for this zinc(II) phthalocyanine based macrocyclic material indicated that this material can be used as a QCM chemical sensor element for chloroform sensing devices with a low detection limit, fast response and recovery times, selectivity, and high sensitivity.

1. Introduction

Volatile organic compounds (VOCs) are a significant class of atmospheric pollutants due to their critical chemical properties, such as a high vapor pressure at ordinary temperature, high reactivity, volatility, and toxicity [1,2]. Many of these chemical materials pose an irreversible threat to human health and the environment. To address these critical issues, it is necessary to develop VOC sensors with high accuracy and sensitivity.

The development of organic materials-based VOC sensing devices has not received adequate attention in the past despite their versatile chemical properties as well as a simple and low-cost production route [3]. Phthalocyanine (Pc) and metallophthalocyanine (MPc) materials have only recently been used as active layers for VOC detection due to their unique properties, such as large spectral shifts upon ligand binding,

intense coloration, and open coordination sites for axial ligation [4]. Pc and MPc are deeply blue-green-colored porphyrinoidic materials containing 18 π-electron conjugated ring systems with four nitrogen atoms in the central cavity [5]. These materials, which can be functionalized via non-toxic aromatic macrocyclic molecules due to their large conjugated π-electron system, have a wide range of applications, including liquid crystals, photovoltaic and solar cells, photosensitizers for photodynamic therapy (PDT), dyes and pigments, and so on [6–9]. Macrocycles have also shown interesting applications such as gas adsorption or separation and VOC detection [10]. The applications of VOC detection with macrocyclic moieties offer a large scale potential of development due to the key-lock conventions with macrocyclic and VOC molecules [11]. Alkoxy and phenyl-thio groups as a typical electron donating and electron-withdrawing substituents at the peripheral position of the phthalocyanine macrocycle can be interesting for gas sensing abilities.

Macrocyclic molecules, such as MPc, changing the macrocycle structure the peripheral substituents or the central metal ion could modify the gas sensing properties [12].

Pc and MPc are also good semiconductor materials and chemiresistive gas sensors due to their planar aromatic ring system, high chemical and thermal stability, chemical functionality and optical absorption as well as their sensing abilities [13,14]. Therefore, these materials contain a wide range of sensor applications such as solid state ionic and capacitance sensors, field-effect transistors (FET), optical gas sensor [15], highly mass-sensitive sensors using a surface acoustic-wave (SAW) or QCM sensors [16]. Some studies in the literature have been actualized related on chemical sensing properties whether by using the peripheral substituent groups or by changing the central metal atom in the Pc core [17–19]. The availability of π-electrons encourages interaction with varied analysts including liquids or gases [20], which causes to detectable changes in the physical or chemical properties of these materials such as mass changes [19], electrical [20] and optical sensing properties [21]. The results of the interactions between the gas molecules and the Pc or MPc materials can be categorized in terms of reversible physical or chemical response, irreversible chemical change or bulk adsorption.

After the discovery of the electronic properties of thin films prepared with Pc and MPc-based materials, they have been utilized in gas sensing applications because they are highly impressed with the adsorption of reducing or oxidization gases [22,23]. CuPc has gained prominence as a precursor material for organic semiconductors due to its excellent film growth and outstanding electronic properties [24].

A variety of techniques, including Spin Coating, Self-Assembled, and Langmuir-Blodgett (LB) technology, can be used to deposit a sensitive organic layer on a suitable solid substrate in the field of bio- and gas sensor applications [15,16,25–27]. The LB technology enables the creation of a controllable single-layer/multilayer film as well as the construction of molecular structures [28]. Thin films of 2, 9, 16, 23-tetra-octyloxy copper phthalocyanine ($CuPcA_8$) and 2, 9, 16, 23-tetra-hexadecyloxy copper phthalocyanine ($CuPcA_{16}$) functionalized with tetra-octyloxy and tetra-hexadecyloxy copper phthalocyanines, respectively, were prepared using the LB technique for the study of the gas-sensing properties against VOCs. The response of the $CuPcA_{16}$ LB film was faster than that of the $CuPcA_8$ LB film because of the effect of sterical hindrance. It was concluded that the substituent groups have a significant impact on the response and recovery properties of MPcs [29].

The sensing properties of zinc and copper(II), functionalized with octakis(octyloxy) groups, based on two different phthalocyanine derivatives mixed with stearic acid LB films against benzene, toluene, methanol, ethanol, chloroform, dichloromethane, carbon tetrachloride vapors were investigated using QCM measurement technique [15]. It is reported that the relatively high responses for chloroform and dichloromethane vapors are attributed to a dipole/dipole interaction or hydrogen bonding between MPc/stearic acid LB film sensor and vapors. Because carbon tetrachloride lacks a dipole, its response was slightly lower than that of dichloromethane and chloroform vapors. The MPc/stearic acid LB film sensor responses observed for benzene and toluene using QCM technique have a lower than other three vapors.

Thin films of [2,9,16,23-tetra-(4-(6-carboxy-2-naphthoxy)-phthalocyaninato-M)] [M = Co(II), Zn(II), Ni(II), Cu(II)] were prepared on the interdigitated electrodes by spin coating technique as active layers to investigate the influence of the central metal atom on the ethanol VOC sensing properties [30]. Similar sensing measurements were reported by Günay et. al for the spin coated films of [(4-(hydroxymethyl)-2,6-dimethoxyphenoxyl)] substituted zinc(II), cobalt(II) and iron(II) phthalocyanines to examine the Pc central metal ion effect on the sensing properties of four main groups of VOCs (chlorinated hydrocarbons, amines alkanes and alcohols) [31]. These studies have proved that the central metal atom plays a significant role in the interactions of VOCs sensing. The insertion of a central metal ion or the addition of additional substituent groups was found to change the

sensing properties of the Pc material. Studies showed that the detection limits, sensitivity and selectivity of gas sensing properties changed when the metal ions or different substituted groups were added to the Pc structure [17,32].

The phthalocyanines, on the other hand, have the disadvantage of low solubility in common organic solvents [33,34]. The solubility of phthalocyanines in these solvents is an important spectroscopic and application parameter for PDT and LB film applications [35,36]. Making suitable substitutions on the aromatic ring, such as 15-membered dioxa-dithia macrocyclic moieties, can greatly improve the solubility of phthalocyanines [37–39].

The present study investigates the synthesis and characterization of a novel phthalocyanine zinc(II) complex containing 15-membered dioxa-dithia macrocyclic moieties (ZnPc), as well as its sensor capabilities against vapors of chloroform, carbon tetrachloride, benzene and toluene at room temperature. The LB film deposition technique was employed to prepare thin films, and the deposition process was monitored using the LB film transfer procedure and QCM measurements. The sensing capabilities of **ZnPc** were investigated using a highly mass change sensitive QCM technique, and the results demonstrated that ZnPc is a promising material for VOC sensing at room temperature.

2. Experimental details

2.1. General

^{1}H NMR, and ^{13}C NMR spectra of novel compounds were measured by a Varian Mercury 400 and Varian Mercury plus 300 MHz NMR spectrometers. UV–vis and FT-IR spectra of compounds were measured were by Schimadzu UV-1601 spectrophotometer, and Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique, respectively. Mass spectra were determined on a Bruker Daltonicis Microflex Mass Spectrometer. Melting points of new compounds were determined on an electrothermal apparatus. {2-[3-(2-iodomethylphenoxy) propoxyl] phenyl}methanol was prepared according to the literature [40]. All used reagents purchased from commercial suppliers and solvents were dried over standard procedures [41].

2.2. Synthesis

2.2.1. Synthesis of S,S-{[propane-1,3-diylbis(oxy)]bis(2,1-phenylene)} diethane thiolate (2)

A suspension of {2-[3-(2-iodomethylphenoxy)propoxyl]phenyl} methanol (**1**) (2.032 g, 4 mmol) and freshly prepared potassium thioacetate (1.824 g, 16 mmol) in dry acetone (150 mL) was refluxed under argon atmosphere for 6 h. This reaction was monitored via TLC [silica gel (chloroform)]. At the end of this period, the reaction mixture was cooled to room temperature and evaporated to dryness. Then the residue was mixed with water and extracted with chloroform (3 × 50 mL). Combined organic phase was dried over anhydrous $MgSO_4$ to give colorless solid, Yield: 1.59 g (98.39%), mp: 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 6.82 (m, 4H, Ar-H), 4.18 (t, 4H, OCH_2), 4.05 (s, 4H, SCH_2), 2.24 (m, 2H, CH_2), 2.16 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.68 (C=O), 156.55, 130.55, 128.76, 125.82, 120.54, 111.21, 64.25 (OCH_2), 30.28 (SCH_2), 29.23 (CH_2), 28.82 (CH_3). FT-IR (ATR, cm^{-1}): 3072, 3038, 2942–2875, 1681 (C=O), 1599–1586, 1493, 1454, 1243, 1104. ESI MS m/z: 404.526 $[M]^+$, 421.428 $[M+H_2O-H]^-$. Anal. calcd. for $C_{21}H_{24}S_2O_4$: C, 62.35; H, 5.98. Found: C, 62.53; H, 6.15.

2.2.2. Synthesis of {[propane-1,3-diylbis(oxy)bis(2,1-phenylene)]} dimethanethiol (3)

Water (4.70 mL) and concentrated H_2SO_4 (4.70 mL) were added to the suspension of compound (**2**) (2.42 g, 6 mmol) in methanol (25 mL) at room temperature under argon atmosphere. The reaction mixture was refluxed for 5 h and monitored with TLC [silica gel (chloroform)]. The

end of this period, reaction mixture was cooled to room temperature and poured into water (85 mL). The mixture was extracted with diethyl ether (3 × 60 mL). The organic phase was separated and washed with water (2 × 60 mL) and dried over anhydrous $MgSO_4$ and then evaporated to dryness under reduced pressure. Colorless solid, yield: 1.72 g (89.58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.19 (m, 4H, Ar-H), 6.88 (m, 4H, Ar-H), 4.24 (t, 4H, OCH_2), 3.72 (d, 4H, SCH_2), 2.33 (m, 2H, CH_2), 1.86 (t, 2H, -SH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.22, 129.93, 129.62, 128.72, 121.04, 111.70, 64.71(OCH_2), 24.21 (CH_2), 24.19 (SCH_2). FT-IR (ATR, cm^{-1}): 3064 (Ar-H), 3038 (Ar-H), 2935–2877 (CH_2), 2564 (S-H), 1598, 1587, 1491, 1453, 1237, 1108. ESI MS m/z: 343.412 $[M+Na]^+$. Anal. calcd. for $C_{17}H_{20}S_2O_2$: C, 63.72; H, 6.29. Found: C, 63.54; H, 6.45.

2.2.3. 13,14-dihydro-6H,12H,20H-tribenzo[f,j,n][1,5]dioxa[9,12] dithiacyclopentadecine-2,3-dicarbonitrile (5)

A suspension of Cs_2CO_3 (1.71 g, 5.25 mmol) in dry DMF (200 mL) was placed under argon and at room temperature in a 500 mL round-bottom three necked flask. A solution of 4,5-dichloro phthalonitrile (0.52 g, 2.625 mmol) in dry DMF (30 mL), and another solution of and compound **3** (0.84 g, 2.625 mmol) in dry DMF (30 mL) were added via a syringe-pump system. The reaction mixture was then stirred at 50 °C for 30 h. The reaction was then monitored by TLC [silica gel (chloroform: hexane) (98:2)]. The reaction mixture was evaporated to dryness and solved in dichloromethane (100 mL) and then washed with 0.10 M NaOH solution (2 × 30 mL). After the separation of organic phase, this dichloromethane solution was washed with water and dried over anhydrous $MgSO_4$ overnight and then evaporated under reduced pressure. Colorless solid, yield: 0.40 g (34%), mp: 213–214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (s, 2H, Ar-H), 7.35 (d, 2H, Ar-H), 7.01 (s, 2H, Ar-H), 6.93 (m, 2H, Ar-H), 6.91 (d, 2H, Ar-H), 4.18 (t, 4H, CH_2O), 4.08 (s, 4H, SCH_2), 2.19 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.12, 145.60, 133.75, 130.94, 126.57, 124.89, 121.74, 115.16, 114.56 (C≡N), 112.47, 66.14, 32.82, 29.81. FT-IR (ATR, cm^{-1}): 3066 (Ar-H), 3042 (Ar-H), 2956–2892 (CH_2), 2226 (C≡N), 1598, 1564, 1494, 1454, 1250, 1107. MS m/z: 444.067 $[M]^+$. Anal. calcd. for $C_{25}H_{20}N_2S_2O_2$: C, 67.54; H, 4.53; N, 6.30. Found: C, 67.36; H, 4.69; N, 6.11.

2.2.4. Synthesis of ZnPc

In a Schlenk system, compound (**5**) (0.276 g, 0.624 mmol), anhydrous $Zn(CH_3COO)_2$ (0.0416 g, 0.226 mmol) and DBU (12 drops) in dry n-pentanol (5 mL) was stirred under reflux for 24 h. This reaction was monitored by TLC [silica gel (chloroform)]. After allowing the mixture to cool to room temperature, it was poured into hexane (40 mL) for precipitation, and the reaction mixture was filtered off. The solid product was purified by column chromatography technique [silica gel (chloroform)] to yield a dark green solid product. Yield: 0.036 g (12.54%), mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.74 (8H, s, Ar-H), 7.41 (m, 8H, Ar-H), 7.22 (m, 8H, Ar-H), 7.01 (m, 8H, Ar-H), 6.93 (m, 8H), 4.25 (m, 16H, OCH_2), 4.08 (m, 16H, SCH_2), 1.21 (m, 8H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.64, 154.86, 145.82, 131.34, 130.80, 125.95, 123.94, 121.60, 115.40, 108.74, 66.86, 32.55, 24.50. UV–vis ($CHCl_3$): λ_{max} (log ε): 711 (5.01), 642 (4.35), 369 (4.79), 285 (4.86). FT-IR (ATR, cm^{-1}): 3059 (Ar-H), 3026 (Ar-H), 2925–2874 (CH_2), 1646 (C=N), 1589, 1489, 1453, 1237, 1104. MS MALDI-TOF m/z: 1842.539 $[M+H]^+$. Anal. calcd. for $C_{100}H_{80}N_8S_8O_8Zn$: C, 65.15; H, 4.37; N, 6.08; Zn, 3.55. Found: C, 65.31; H, 4.57; N, 5.90, Zn, 3.33.

2.3. LB thin film preparation

As an LB film material, zinc(II) phthalocyanine-based macrocyclic molecules were dissolved in chloroform at a concentration value of 1 mg/mL. After cleansing the water surface, a predetermined volume (500 μL of this prepared solution was spread very slowly as droplets onto the water surface using a Hamilton syringe. The solvent (chloroform)) was allowed to evaporate for 5–20 min. Molecules were discovered in a random distribution on the water surface, indicating that their

interaction with one another is minimal. Subsequently, the distance between the movable barriers in the trough is gradually reduced in order to reduce the surface area and study the behavior of molecules floating on the water surface. The molecules on the water surface approach each other and begin to interact as the surface area of the water decreases. The surface pressure sensor (Wilhelmy balance) was used to measure these interactions, yielding a measurement of the change in surface pressure (π) versus surface area (A). The π-A plot obtained in the LB film technique is called the isotherm graph and shows the characteristic behavior of the monolayer at the air-water interface.

When the barriers are fully open, the interactions between floating phthalocyanines at the water surface are very weak, and the measured surface pressure is close zero. This is known as a gas phase on the isotherm graph. If the barrier continues to compress the monolayer on the water surface, π value gradually increases while surface area decreases. This corresponds to the so-called liquid phase. As the monolayer is compressed further, a regular molecular architecture is formed, which is ideal for thin film production (solid phase). Intermolecular interactions occur at the highest level and surface pressure increases rapidly while change in surface area remains almost constant. LB thin film production is carried out at values in the solid phase pressure range. The regular structure of the single layer floating on pure water is disrupted if the barrier continues to compress. A rapid drop in surface pressure is observed in this case, and a regular monolayer collapses. The isotherm graph is used to examine the behavior of the single layer floating on pure water and to determine the surface pressure that must be maintained during thin film production.

In this study, LB thin film coating technique was used to produce Y-type thin films. In the LB thin film coating method for Y-type deposition, molecule attachment is provided to the solid substrate surface both during its orientation from air to water and from water to air.

It is necessary to calculate the transfer ratio (TR) defined by Eq. (1) in order to clearly state whether the transfer process is performed regularly or not [42].

$$TR = \frac{A_1}{A_2} \tag{1}$$

A_1: reduction in the area of a single layer on the pure water surface, A_2: the area covered by a single layer transferred onto the substrate. The TR parameter for LB thin films is in the range of $0 \leq TR \leq 1$. For a regular LB film, this range is considered to be 0.9–1.

2.4. QCM technique

In this work, a quartz crystal (3.5 MHz) which was sandwiched between two electrodes was used for QCM measurements. The mechanism of QCM measurement can be simply clarified that the mechanical power can be obtained in case the electrodes of the crystal was exposed to the electrical power because of the piezoelectric effect. In this way, the resonance frequency was produced by QCM crystal through an oscillator circuit. This frequency is proportional to the mass accumulated on the QCM surface. The relation between the mass accumulated on the surface and the frequency is expressed by the Sauerbrey equation [43]. Two different characterization studies were performed using the QCM technique. The first study was based on the transferability of **ZnPc** LB thin film monolayers on the QCM substrate during the deposition process. In the second study, the sensor properties of **ZnPc** LB films were investigated by real-time kinetic studies using the QCM technique. A symbolic representation of this technique, which was a home-made designed, was presented in Fig. S19 and the detailed information about this system were presented in supplementary information.
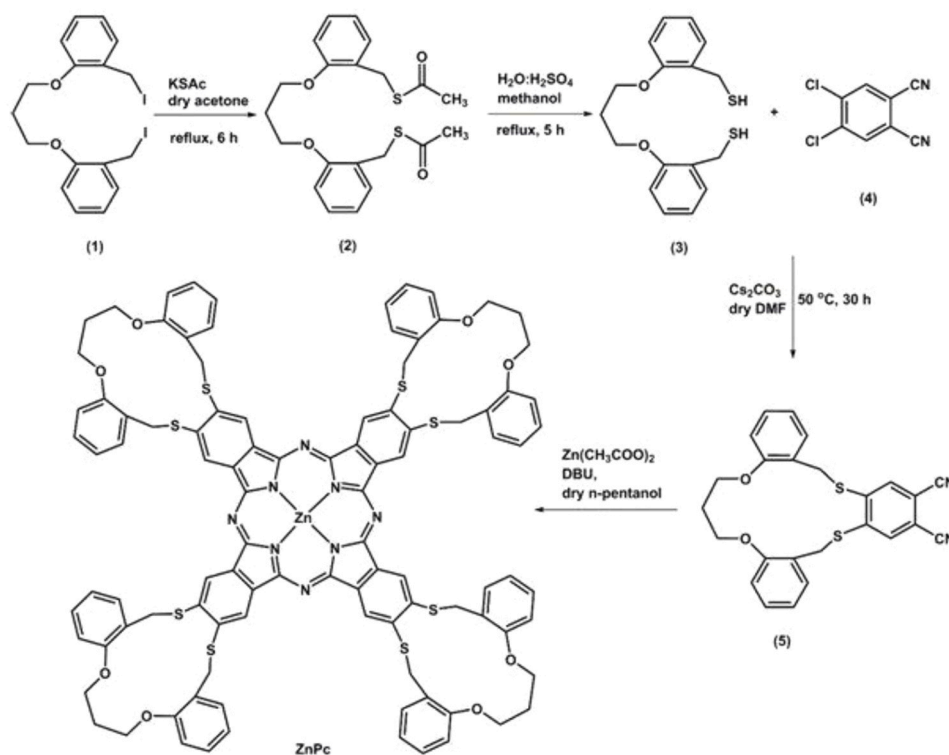
Scheme 1. Synthetic route of **ZnPc**.

3. Result and discussion

3.1. Synthesis and structural characterization of materials

The synthetic pathway of new phthalocyanine zinc(II) complex containing 15-membered dioxadithia macrocycle moieties were given at Scheme 1. One of the precursor compound (**2**) was synthesized from {2-[3-(2-iodomethylphenoxy)propxy]phenyl} methanol [6] and freshly prepared potassium thioacetate in very high yield (98.39%). The FT-IR NMR and MS spectra of compound **2** were significant as expected. The ^{1}H, ^{13}C NMR and FT-IR spectra of **2** showed the characteristic chemical shifts for CH_3 protons, carbonyl resonances for C=O moieties and stretching vibrations of the last group at $\delta = 2.16$, 195.68 ppm and 1681 cm^{-1}, respectively (Figs. S3, S4, S1). The appearance of these peaks confirms the completion of esterification reaction. In addition, ESI mass spectra of this compound at $m/z = 404.526$ [M]$^+$ also supported the proposed structure (Fig. S2). The hydrolysis reaction of compound **2** was performed in H_2O/H_2SO_4 (1/1) media at reflux condition in high yield (89.58%). The disappearance of resonances related acetate group protons at $\delta = 2.16$ ppm, carbonyl groups chemical shifts at $\delta = 195.68$ ppm and appearance of novel resonances at $\delta = 1.86$ ppm as a triplet concerning –SH moieties also confirmed the new formation of compound **3** (Fig. S7, Fig. S8). The disappearance of C=O and appearance of –SH stretching vibrations at 2564 cm^{-1} were also supported the hydrolysis reaction (Fig. S5). In addition to that, the ESI mass spectrum of this compound at $m/z = 343.412$ [M+Na]$^+$ confirmed the proposed structure (Fig. S6). The macrocyclization reaction to obtain compound **5** was performed in DMF medium between compound **3** and 4,5-dichlorophthalonitrile (**4**) by using high dilution technique in 34.32% yield. The disappearance of resonances concerning –SH protons at $\delta = 1.86$ ppm and appearance of novel chemical shifts at $\delta = 7.54$ ppm as singlet related to new aromatic proton resonances in ^{1}H NMR spectrum of compound **5** was supported the proposed formulation (Fig. S11). The novel characteristic chemical shifts related C=N moieties at $\delta = 114.56$ ppm in ^{13}C NMR spectrum of this compound also confirmed

the 15-membered dioxa-dithia macrocycle formation (Fig. S12). This macrocycle (**5**) displayed, the molecular ion peak at $m/z = 444.067$ [M]$^+$ (Fig. S10). The appearance of new stretching vibrations related C≡N moieties in FT-IR spectrum of this compound at 2226 cm^{-1} also confirmed the macrocyclization reaction has been achieved (Fig. S9).

Phthalocyanine **ZnPc** was prepared in 12.54% yield by refluxing phthalonitrile (**5**) and anhydrous zinc(II) acetate in dry n-pentanol in the presence of DBU for 24 h. In the ^{1}H NMR spectrum of **ZnPc**, the signals for -OCH$_2$, -SCH$_2$, -CH$_2$ and aromatic protons resemble those of the precursor phthalonitrile (**5**) (Fig. S15). The disappearance of C≡N resonance belonging to the dinitrile compound at $\delta = 114.56$ ppm and appearance of novel chemical shifts at $\delta = 154.86$ ppm related C≡N moieties in the ^{13}C NMR spectrum of **ZnPc** indicated the formation of zinc(II) phthalocyanine was achieved (Fig. S16). In addition to that, cyclotetramerization reaction of phthalonitrile (**5**) was confirmed by the disappearance of the characteristic C≡N stretching vibrations in the FT-IR spectrum of **ZnPc** (Fig. S13). The elemental analysis and ESI mass spectrum data of **ZnPc** by the presence of molecular ion peak at $m/z = 1842.539$ [M+H]$^+$ confirmed the **ZnPc** structure (Fig. S14). We observed the significant absorptions concerning to the Q-bands at 711 nm and Soret-like bands near at 369 nm in the UV–vis spectrum of this compound in chloroform (Fig. S17). The single narrow absorption at the Q band region of metallophthalocyanine should be related to the π →π * transition of the completely conjugated 18π electron system [44, 45]. This single absorption is due to its D_{4h} symmetry and the fact that the metallophthalocyanine is not aggregated [46].

3.2. Fabrication of the ZnPc LB films and isotherm graph

NIMA 622 model LB trough was used for the production of multilayer LB thin film by transferring the monolayer at the air-water interface onto the solid substrate (quartz crystal). The Langmuir properties of the single layer floating at this interface were investigated with the help of the π-A isotherm plot. The isotherm curve of the **ZnPc** molecule with 1841.54 g mol^{-1} molecular weight and 1 mg/mL solution concentration
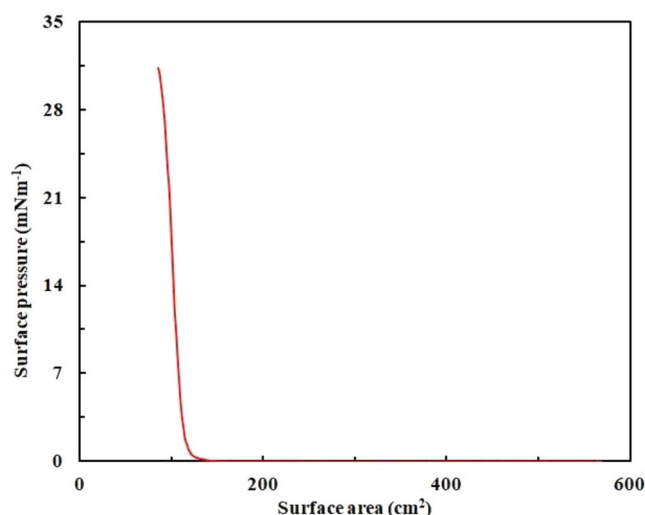
Fig. 1. Isotherm graph of **ZnPc** at the air-water interface.

is shown in Fig. 1 for 500 µl volume. While solid phase, liquid phase and gas phase regions were observed in the isotherm ensured as a result of compression of the **ZnPc** single layer at the interface between air and water. Barrier speed was determined as 200 cm^2 min^{-1} in the experiments.

After the solution of **ZnPc** prepared by dissolving 10 mg **ZnPc** materials in 10 mL chloroform was organized at the air-water interface, the appropriate pressure value for transfer was determined from the solid phase range with the help of the isotherm curve. The transfer pressure value was chosen as 21 mN m^{-1}. A symmetrical Y-type LB thin film was produced from a monolayer of **ZnPc**. Transfer speed was determined as 25 mm min^{-1} in experiments. QCM method was employed to test the transfer process is successful or the LB film structure is regular. Transfer graph of 2 layer **ZnPc** LB thin film production is given in Fig. 2. At point **a**, the surface area begins to decrease as the transfer process takes place

when the substrate touches the single layer on the pure water surface. This process onto QCM substrate continues until point **b**. At point **b**, the QCM substrate is completely into the pure water. In the process from point **b** to point **c**, the substrate moves from the pure water to the air environment. At point **c**, the substrate is completely separated from the pure water. This process was applied until the 10 layer transfer process of **ZnPc** material was completed. Using Fig. 2 and Eq. (1) the transfer ratio is calculated as TR > 0.94. This high TR value indicates that the LB thin film layers were transferred regularly in the course of the deposition process belong to **ZnPc** single layer.

3.3. Characterization of ZnPc LB thin films

In this represented work, **ZnPc** thin films were prepared in a symmetrical mode, which comes forward with the fame as the Y-type LB film, onto QCM substrate. Fig. 3 shows the frequency change versus the number ZnPc LB of layers deposited onto QCM crystal. This linear relationship with a regression value of 0.9899 indicated that ZnPc LB layers were successfully fabricated and that the mass of each transferred layer remained almost the same during the deposition process. The frequency change value is 23.24 Hz per layer and the mass (377.98 ng/layer) for each layer coated onto the substrate were provided from the data given in Fig. 3 as well as utilizing Sauerbrey equation [43].

Characterization of **ZnPc** LB thin films is also carried out by using UV–vis spectrophotometer to control the fabrication of multilayer **ZnPc** LB thin film onto quartz glass substrate. The UV–vis absorption spectra of **ZnPc** LB films prepared onto a quartz glass with different layers (2, 6 and 10 layers) is given in the Fig. S18. The relationship between UV-absorbance and **ZnPc** LB films (at 310 nm) was also presented in the inset of the Fig. S18.

3.4. Kinetic results

The detection kinetics of some selected VOCs were investigated systematically using real-time monitoring of the frequency change in the QCM sensor surface coated with 10-layer **ZnPc** LB films. The induced transient responses were recorded in all measurements when the sensor
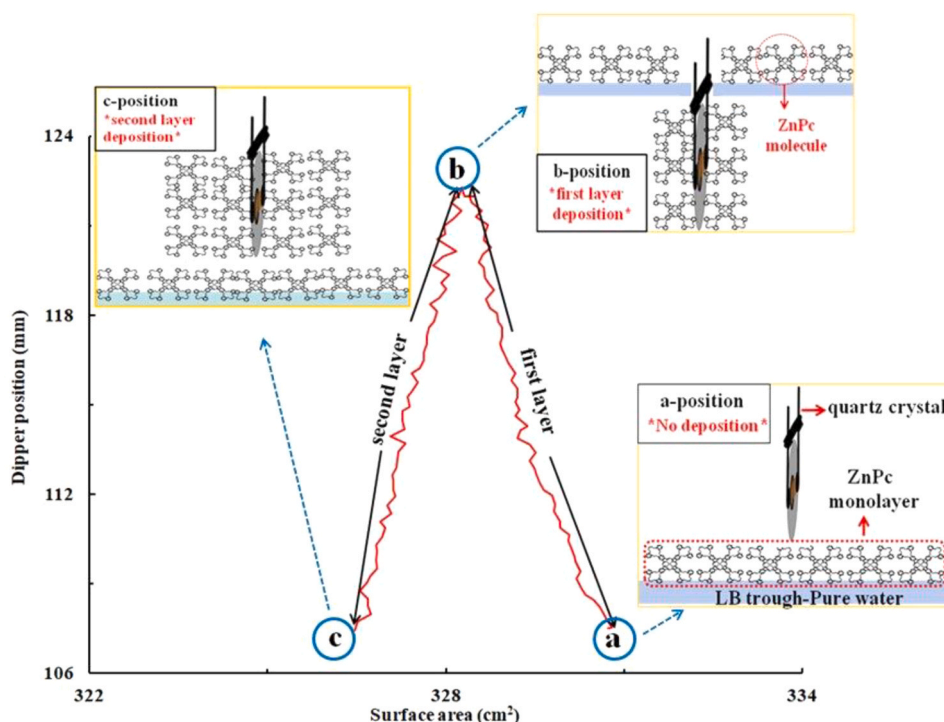

Fig. 2. Deposition process of **ZnPc** LB thin film onto a quartz crystal substrate.
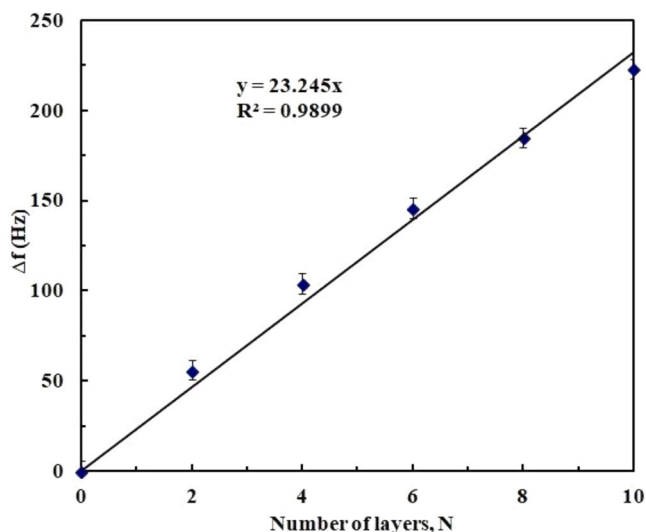
Fig. 3. Linearity of the frequency change versus the number ZnPc LB of layers deposited onto QCM crystal.

was alternately exposed to target vapor and fresh air. Transient responses after 2 min of alternating chloroform and fresh air exposure are shown in Fig. 4. Fresh air is injected into the QCM chamber first, causing virtually no change in frequency, followed by chloroform exposure, which leads adsorption and diffusion, and then fresh air is re-injected into the test chamber for sensor recovery. When the **ZnPc** QCM sensor is exposed to chloroform, it undergoes an abrupt change in frequency due to the adsorption process, followed by an exponential reduction with the beginning of the diffusion process. This sudden and rapid change is caused by surface interaction between the **ZnPc** LB film surface and chloroform molecules. Fig. 5 depicts QCM-kinetic measurements on chosen VOCs (carbon tetrachloride, benzene, and toluene) for comparison.

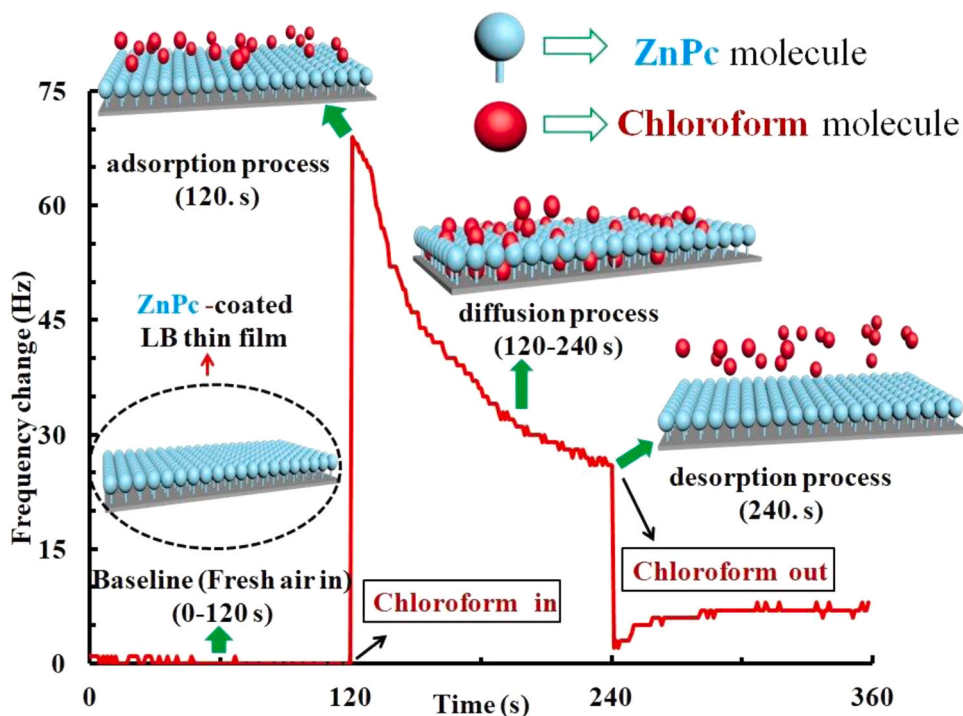QCM measurements indicate that remarkable and comparatively

larger response values are obtained for chloroform amongst other vapors used at 15 ppm concentration (given in Fig. 5). In accordance with the purpose of observing the repeatability and renewability features of the **ZnPc** LB film chemical sensor, in Fig. 6, the QCM kinetic data of the related sensor against chloroform vapor that was obtained as a result of three repetitive experiments was presented. In light of this kinetic information, it is clear that the QCM-sensor of **ZnPc** is reproducible for chloroform vapor. Accordingly, as represented in Fig. 7, the interactions were recorded for a variety of chloroform concentrations.

It is clear that the frequency changes of the **ZnPc** QCM-sensor for all VOCs follow the following order: toluene < benzene < carbon tetrachloride < chloroform. This can be clarified by the differences in the physical properties of VOCs (given in Table 1) such as vapor pressure, dipole moment, molar volume and molecular weight, which have been
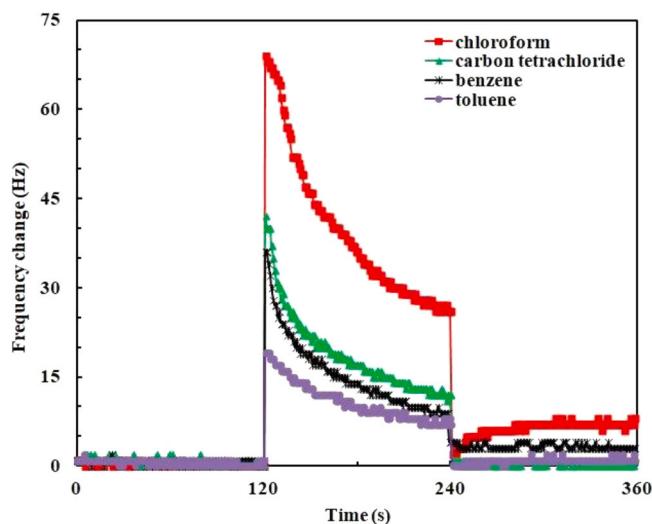

Fig. 5. The **ZnPc** QCM sensor-VOCs kinetic measurements for four different vapors at concentration of 15 ppm.
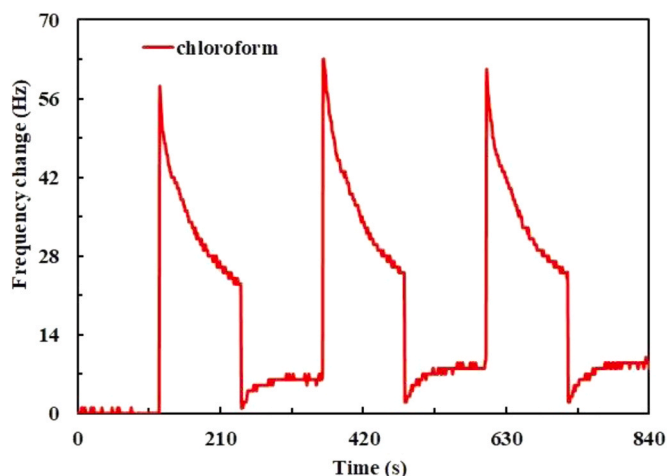

Fig. 4. Schematic representation of the sensing mechanism of the ZnPc-QCM sensor.

Fig. 6. The repeatability and renewability properties of **ZnPc**-QCM sensor at concentration of 15 ppm of chloroform.
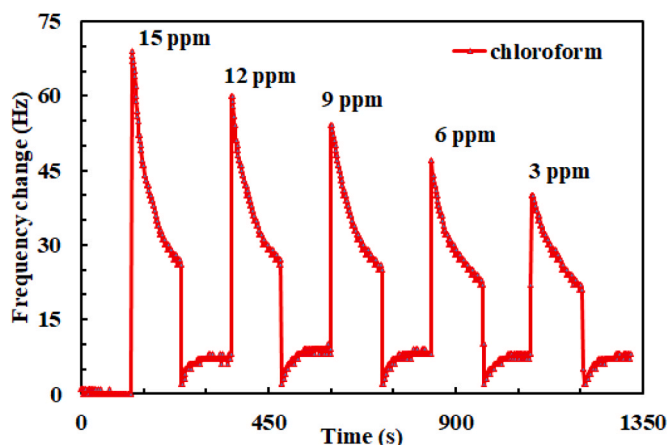

Fig. 7. Behavior of the **ZnPc** QCM-sensor at different concentrations of chloroform over time.

reported in previous studies [47–49].

Since chloroform molecules have the highest dipole moment and vapor pressure while having the lowest molar volume when compared to other vapors, they are introduced into the **ZnPc** QCM-sensor film more easily and quickly. Because of these physical properties influencing the sensor-vapor interaction, the responses of this mass-sensitive chemical sensor in terms of frequency change for the other VOCs (benzene, carbon tetrachloride, and toluene) are lower than chloroform vapor.

When compared to the diffusion of chloroform vapor into the same thin film, the other VOCs have higher molar volumes and can hardly diffuse into the ZnPc-based thin film, according to these kinetic results. The lower response recorded for carbon tetrachloride vapor in comparison with chloroform vapor may also be examined in terms of dipole moment (this VOC has no dipole moment). The interaction between the **ZnPc** sensor molecule and carbon tetrachloride molecule is estimated to stem from electrostatic interactions. The relatively high molecular

weight of carbon tetrachloride with respect to chloroform and other VOCs should be considered. Due to its high molecular weight and its voluminous size, the carbon tetrachloride molecule may have difficulty penetrating the ZnPc LB film [15,50]. However, the frequency shift of the ZnPc QCM-sensor towards this vapor is greater than benzene and toluene VOCs. It can be clarified with the vapor pressures of these VOCs, and it is well known that higher vapor pressure leads to a larger response [47].

The data in Fig. 7 was utilized to state the values of two important parameters (the sensitivity and the LOD) of the ZnPc QCM-sensor for chloroform vapor. A proportion of $\Delta f/c$ is usually described as sensitivity (S) for QCM sensors. Δf (Hz) and c (ppm) represent the frequency change and the concentration, respectively. Fig. 8 displays that a linear relationship is observed between Δf and c. This means that more chloroform vapor molecules would be adsorbed onto the QCM-sensor modified with a multilayer ZnPc LB film, when the number of penetrated chloroform vapors into the gas cell increases. From the slope of this linear graph, the sensitivity value of the ZnPc QCM-sensor is calculated as 2.6 Hz ppm^{-1} for chloroform vapor.

The limit of detection (LOD) can be obtained via Eq. (2) from the standard deviation (σ) and slope of the plot in Fig. 8.

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

The LOD value is calculated as 1.2 ppm by Eq. (2), for the QCM-sensor modified with **ZnPc**. Also, the sensitivity values of 2.1, 1.9 and 1.6 Hz ppm^{-1} for **ZnPc** QCM-sensor were obtained with the LOD values of 1.4, 1.5 and 1.9 ppm for carbon tetrachloride, benzene and toluene vapors, respectively. Also, the results of the Pc-based QCM response to some VOCs were compared with our previous results, which are in the literature and given in Table S1.

As a summary of the sensing measurements, the ZnPc QCM-sensor is considered to be a promising alternative for detecting chloroform vapor due to its high sensitivity, fast response and recovery times, selectivity,
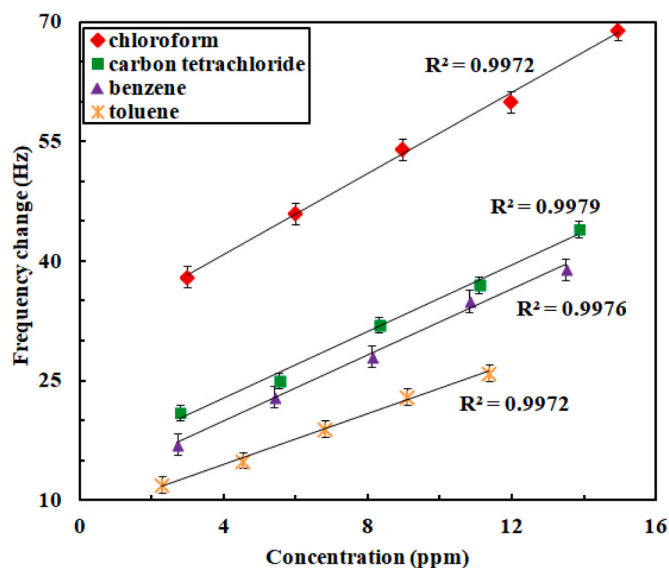

Fig. 8. Frequency shifts versus concentrations of organic vapors.

Table 1

The responses of **ZnPc** QCM-sensor and some physical properties of organic vapors.

Organic vapors	Molar volume (cm^3 mol^{-1})	Vapor pressure (kPa, 20 ℃)	Dipol moment, (D)	Molecular weight (g mol^{-1})	Frequency shift, (Δf)
Chloroform	80.70	21.00	1.08	119.38	69
Carbon tetrachloride	97.10	12.00	0	153.82	41
Benzene	86.36	9.95	0	78.11	35
Toluene	107.00	2.91	0.36	92.14	18

and low LOD. In this context, a novel ZnPc material can be presented as an alternative mass-sensitive sensor element for detecting chloroform vapor at room temperature.

4. Conclusions

In this work, a novel phthalocyanine zinc(II) complex containing 15-membered dioxa-dithia macrocyclic moieties (**ZnPc**) was successfully synthesized and characterized to investigate its chemical sensor abilities. **ZnPc** QCM-sensor was prepared by producing **ZnPc** LB thin film onto QCM and the transfer pressure value of 21 mN m^{-1} was determined a suitable surface pressure during deposition process. The **ZnPc** LB thin film formed with 10 layers was regularly transferred onto the quartz crystal with a high transfer ratio of >0.94. Also, the frequency change and the mass transferred onto the QCM for a single layer could be determined with a linear regression of 0.9899 of 23.24 Hz and 377.98 ng, respectively. Kinetic vapor measurements of the **ZnPc** QCM-sensor were recorded by exposing some aromatic hydrocarbons (benzene and toluene) and chlorine containing aliphatic hydrocarbons (chloroform and carbon tetrachloride) to examine the chemical sensor properties of this novel QCM-sensor. These kinetic findings indicate that a novel zinc(II) phthalocyanine derivative is promising material for QCM VOCs sensor applications at room temperature.

CRediT authorship contribution statement

Yaser Acikbas: Writing – original draft, Writing – review & editing. **Matem Erdogan**: Writing – review & editing. **Rifat Capan**: Writing – original draft, Writing – review & editing. **Cansu Ozkaya**: Writing – original draft. **Yasemin Baygu**: Writing – review & editing. **Nilgün Kabay**: Writing – review & editing. **Yaşar Gök**: Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.synthmet.2021.116870.

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