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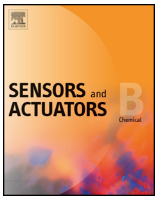

Ethanol sensing property of novel phthalocyanines substituted with 3,4-dihydroxy-3-cyclobuten-1,2-dione

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ABSTRACT

The novel mono metallo [Zn(II) **2a** and Co(II) **2b**] phthalocyanines have been synthesized from compound **1**, which can be obtained by the reaction of 4-nitrophthalonitrile with 3,4-dihydroxy-3-cyclobuten-1,2-dione. The novel mono phthalocyanines with cyclobuten unit have been characterized by elemental analysis, UV–vis, FT-IR, ^{1}H NMR, and mass spectroscopy. The effect of humidity on the ethanol sensing capability of the spin coated lilms **2a** and **2b** has been studied. The results showed that the presence of humidity, acting as interference gas, reduces both sensitivity and response time of the sensors. In addition, studies on response time and repeatability of the sensors have also been carried out. Applications of Elovich and Ritchie kinetic models to adsorption systems were reviewed. Results show that while the Ritchie equation may be applied for low temperature adsorption processes, while Elovich equation generates a straight line that best fit to the data of adsorption of ethanol vapors on Pc films at higher temperature.

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1. Introduction

Phthalocyanines play a major role in modern technology with various applications including catalysis [1], semiconductors and solar cells [2], optical materials [3], photodynamic therapy [4], electrochromic materials [5], gas sensors [6] and component of molecular-based information storage systems [7]. Therefore, various types of phthalocyanines have been reported, including binuclear, binuclear double decker and double decker clamshell, trinuclear, tetranuclear, pentanuclear and octanuclear [8].

Ethanol sensors have wide applications in many fields, such as the control of fermentation processes [9], safety testing of food packaging, medical processes, and can also be fixed on vehicle steering wheels to monitor drunken driving [10,11]. Various chemoresistive metal oxide gas sensors have been used to detect ethanol, which include SnO_2 nanorods [12], activated ZnO [13], Ni doped SnO_2 hollow spheres [14], TiO_2 [15] and MoO_3 [16]. Well known disadvantages of inorganic semiconductor gas sensors are their low selectivity, high operating temperature, long response and recovery time of the sensor signal [17]. However, many organic semiconductor sensors offer a low operating temperature, high gas sensitivity and short response and recovery time. Among organic materials, phthalocyanines are well known for their high sensitivity in the detection of different gases and volatile organic compound vapors such as, CO_2, SO_2, NO_2 and toluene [18–21] thus it has a significant advantage in gas-sensing applications, which have received a fast development in the past decades.

In this study, mono metallophthalocyanines **2a** and **2b** were synthesized by reaction of compound **1** with the respective metal salts in DMF (see Scheme 1). The ethanol sensing properties and the kinetics of adsorption for the **2a** and **2b** coated sensors were investigated as function of temperature and ethanol vapor concentration. The interference between the target and other substance, such as humidity, is typically the problem for a chemical sensor. Therefore, the effect of humidity, functioning as the interference gas, on the response–recovery behavior of the Pc films was also investigated.

2. Experimental

All solvents (reagent grade) and the starting materials were acquired from Sigma–Aldrich and were used without purification.

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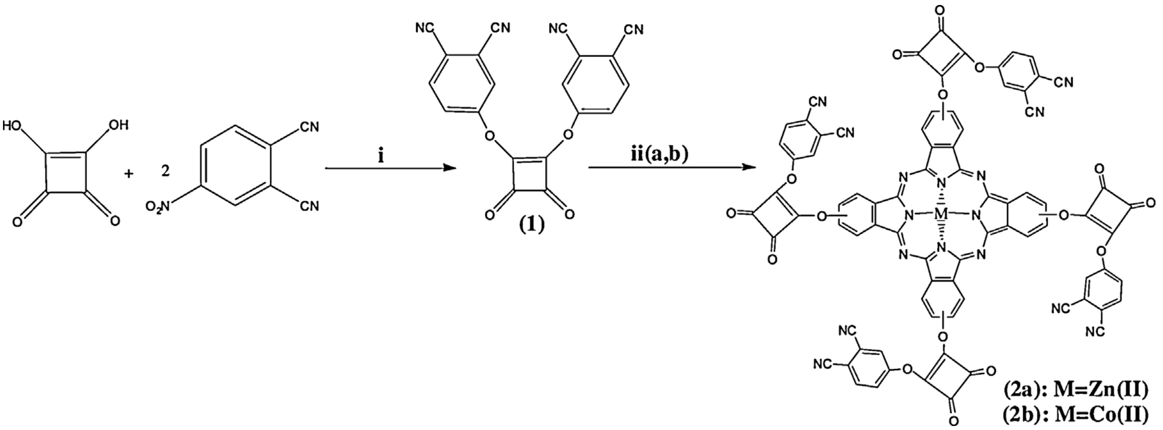

Scheme 1. Summary of the synthesis of all compounds. (i) K_2CO_3, Ar, DMF, 70 °C; (ii) (a) $Zn(OAc)_2{\cdot}2H_2O$, Ar, DMF, reflux, (b) $Co(OAc)_2{\cdot}4H_2O$, Ar, DMF, reflux.

^1H NMR spectra were recorded at 400 MHz on a Bruker 400 spectrometer at room temperature using an internal deuterium lock. Chemical shift values are given in ppm relative to tetramethyl silane (TMS). Quantitative UV–visible spectra were recorded with a Shimadzu UV-1700 spectrometer. IR spectra were recorded on an Ati Unicam Mattson 1000 Series FT-IR spectrometer (KBr pellet). Elemental analyses were performed by the LECO CHNS 932. Mass spectra were acquired on a Voyager-DE™ PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra for **2a** and **2b** were recorded in linear using positive mode with average of 100 shots.

2.1. Synthesis

2.1.1. Synthesis of [4,4′-(3,4-dioxocyclobut-1-ene-1,2-diyl)-bis(oxy)] diphthalonitrile (1)

A mixture of 4-nitro-1,2-dicyanobenzene 1 (3.46 g, 20 mmol) and 3,4-dihydroxy-3-cyclobuten-1,2-dione, 2 (1.14 g, 10 mmol) in 15 mL of dry DMF was stirred at 70 °C under Ar. Anhydrous K_2CO_3 (4.14 g, 30 mmol) was added to the mixture for over a period of 4 h. After stirring the reaction mixture for a further 24 h, the undissolved salt was removed by filtration. The reaction mixture was poured into ***ice*** water (300 mL) and stirred. The pale yellow product was filtered and washed successively with hot water, methanol and chloroform. This compound is readily soluble in the majority of organic solvents such as THF, DMF and DMSO.

Yield; 2.90 g (79%). Mp: 262 °C. IR (KBr pellet) $\nu_{max/cm}{}^1$: 3102–3038 (arom.–H); 2234 (C≡N); 1804 (C=O); 1711 (C=N); 1588–1484 (Ar–C=C); 1253 cm^{-1} (Ar–O–Ar). ^1H NMR (400 MHz, DMSO-d_6): δ, ppm 7.51–8.25 (m, Ar–H). Anal. Calcd. (%) for $C_{20}H_6N_4O_4$: C, 65.58; H, 1.65; N, 15.29. Found: C, 66.01; H, 1.80; N, 15.78%.

2.1.2. 2,10,16,24-Tetrakis[4,4′-(3,4-dioxocyclobut-1-ene-1,2-diyl)-bis (oxy)]phthalocyaninato zinc(II) 2a

A well-powdered mixture of compound **1** (1 g, 2.73 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (0.124 g, 0.68 mmol) were refluxed in 10 mL of dry DMF under argon for 24 h. The reaction mixture was cooled down to room temperature and the undissolved salt was removed by filtration. Then the reaction mixture was poured into ice-water (100 mL) and stirred. The resulting precipitate was filtered and washed with hot water, methanol, chloroform, acetone and acetonitrile to remove the unreacted organic materials, the dark green product was dried. This compound is readily soluble in DMF and DMSO. Yield; 0.31 g (30%). Mp > 350 °C. IR (KBr pellet) $\nu_{max/cm}{}^1$: 3070 (arom.–H); 2232 (C≡N); 1771 (C=O); 1722 (C=N); 1599–1471 (Ar–C=C); 1248 cm^{-1} (Ar–O–Ar). ^1H NMR (400 MHz, DMSO-d_6): δ, ppm 7.48–8.30 (m, Ar–H). UV–vis (DMF), λmax, nm (log ε): 680(4.66), 622(4.20), 350 (4.52). Anal. Calcd. (%) for $C_{80}H_{24}N_{16}O_{16}Zn$: C, 62.77; H, 1.58; N, 14.64. Found: C, 62.50; H, 2.02; N, 14.88%. MS (MALDI-TOF) *m*/*z*: 1531.50 [M+H]+.

2.1.3. 2,10,16,24-Tetrakis[4,4′-(3,4-dioxocyclobut-1-ene-1,2-diyl)bis (oxy)]phthalocyaninato cobalt(II) 2b

Compound **2b** was prepared according to the same procedure as described for the preparation of **2a** by starting from compound **1** (1 g, 2.73 mmol) and $Co(OAc)_2{\cdot}2H_2O$ (0.12 g, 0.68 mmol). The dark green product was filtered and washed with hot water, methanol, chloroform, acetone and acetonitrile to remove the unreacted organic materials. This compound is soluble in organic solvents such as DMF and DMSO.

Yield; 0.28 g (27%). Mp > 350 °C. IR (KBr pellet) $\nu_{max/cm}{}^1$: 3098–3038 (arom.–H); 2232 (C≡N); 1772 (C=O); 1722 (C=N); 1590–1485 (Ar–C=C); 1254 cm^{-1} (Ar–O–Ar). UV–vis (DMF), λmax, nm (log ε): 675(4.96), 611(4.45), 310 (5.35). Anal. Calcd. (%) for $C_{80}H_{24}N_{16}O_{16}Co$: C, 63.04; H, 1.59; N, 14.70%. Found: C, 63.65; H, 1.82; N, 14.98. MS (MALDI-TOF) *m*/*z*: 1525 [M+H]+.

2.2. MALDI sample preparation

MALDI matrix, α-cyano-4-hydroxycinnamic acid (ACCA) was prepared in THF:water mixture in 1:1 (v/v) ratio having 0.1% TFA at a concentration of 10 mg mL^{-1}. MALDI samples for **2a** and **2b** were prepared by mixing sample solutions (0.5 mg/mL in tetrahydrofuran:water mixture:DMSO, 1:1:0.01, v/v having 0.1% TFA) with the matrix solution (1:10, v/v) in a 0.5 mL eppendorf® micro tube. Finally 0.5 μL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

2.3. Ethanol sensing measurements

Thin films of the investigated compounds were obtained by spin-coating solutions of the compound over the electrode arrays to obtain devices suitable for gas sensing measurements. The measurement electrodes used in the experiment consist of an interdigital array of metal electrodes photolitographically patterned on pre-cleaned glass substrate. Prior to vacuum evaporation, glass substrates were thoroughly cleaned by ultrasonically and then coated with 100 Å of chromium followed by 1200 Å of gold in an Edwards auto 500 coater system. The film patterned photolitographically and etched to provide 10 fingers pairs of electrodes having a width of 50 μm, spaced 50 μm from the adjacent

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