



Partition coefficient–Lewis basicity correlation in four dioxycyclobutenedion-bridged novel ball-type phthalocyanines



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ARTICLE INFO

Article history:

Received 4 September 2015

Received in revised form 20 November 2015

Accepted 27 November 2015

Available online 11 December 2015

Keywords:

Dioxycyclobutenedion bridged

Ball-type

Phthalocyanine

Partition coefficient

Lewis basicity

Gas sensing

ABSTRACT

The novel ball-type bis-metallo [Zn(II), Co(II) and Cu(II)] phthalocyanines were synthesized from 4,4'-(3,4-dioxocyclobut-1-ene-1,2-diyl)-bis(oxy)] diphthalonitrile, which can be obtained by the reaction of 4-nitrophthalonitrile with 3,4-dihydroxy-3-cyclobuten-1,2-dione. The novel ball-type phthalocyanines with cyclobutene unit were characterized by elemental analysis, UV–vis, FT-IR, ¹H NMR, and MALDI-TOF mass spectroscopy. The response and recovery behaviours of the films to different analytes, which span a broad range of Lewis base, were investigated by utilizing an AT-cut quartz crystal resonator. Frequency changes during transient exposures to these vapours were rapid and reversible. The sensing behaviour of the films for a broad range of Lewis bases and the correlation between the partition coefficients and Lewis base enthalpies were investigated. Partition coefficients obtained from the linear response regimes of the calibration curves were in the 800–22,000 range. Results show that partition coefficients may be correlated exponentially with binding enthalpy.

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1. Introduction

As functional materials, phthalocyanine and many of its derivatives continue to be subject of the increasing research for applications in many areas. Thus, significant attention is drawn to the synthesis of new compounds and their characterization. The chemical and physical characteristic of these compounds may be varied with the central metal ion, peripheral or non-peripheral substitution, and the ligands attached to the central atom [1]. Today, peripherally or non-peripherally substituted derivatives, and about 70 different elements including metals and some metalloids have been used as central atoms in all kinds of phthalocyanines [2]. Nevertheless, ball-type or face-to-face diphthalocyanines are a new class of compound, which was reported in 2002 for the first time [3]. The ball-type phthalocyanines show different and interesting properties, such as electrical, gas sensing, electrocatalytic, and electrochemical [4]. However, these properties of phthalocyanines change significantly due to the distance between the two phthalocyanine monomers [5]. Especially, ball-type cobalt phthalocyanines displayed high catalytic

activity towards dioxygen reduction, which has vital importance in fuel cell applications [6].

In our previous work, [4,4'-(3,4-dioxocyclobut-1-ene-1,2-diyl)-bis(oxy)] diphthalonitrile (1) was prepared and used as a starting material for the preparation of mono metallophthalocyanines substituted with 3,4-dihydroxy-3-cyclobuten-1,2-dione refluxing in DMF. This mono phthalocyanine complexes showed high sensitivity towards ethanol vapour [7]. There is a need for chemical sensors that can detect vapour phase of analytes with sensitivity and selectivity under field conditions. Among the many types of chemical sensors suitable for such an application, quartz crystal resonator (QCR), also known as a quartz crystal microbalance (QCM), becomes a highly sensitive gas sensor when coated with the appropriate materials [8]. When the coated QCM sensor is functioning as a simple mass sensor, then the sensor's shift in resonance frequency on exposure to the organic vapour is related to mass change (Δm). The quantitative relationship between the negative frequency shift and the mass loading on the QCM surface was derived by Sauerbrey [9] for the first time as follows:

$$\Delta f = -2.26 \times 10^6 f_0^2 \frac{\Delta m}{A} \quad (1)$$

where Δf is the measured frequency shift, f_0 is the fundamental frequency of the bare piezoelectric crystal, A is the surface area of the electrode, and Δm is the change in mass on the surface of the

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quartz crystal. Hence, the frequency shift is directly proportional to the adsorbed mass on the coated QCM transducers. The sensing behaviour of many metallophthalocyanines to various analytes, including strongly basic analytes, such as pyridine [10], polar protic solvents [11,12], aromatic compounds [13], and strong oxidants, such as NO and NO₂ [14,15]. However, little previous work has been done on analytes with a broad range of binding strengths.

In this study, from the same starting material **1**, the ball-type phthalocyanines **2**, **3**, and **4** were synthesized by heating with metal salts in the medium without solvent (see Scheme 1). The new ball-type phthalocyanines were obtained in sufficient purity after washings with different solvents and then characterized by spectroscopic methods. The partition coefficients for the sorption of the selected analytes by **2**, **3**, and **4** thin films on QCM transducer were obtained and the relation between the partition coefficients and Lewis basicities of analytes was examined.

2. Experimental

2.1. Materials

All solvents (reagent grade) and the starting materials were acquired from Sigma–Aldrich and were used without any purification. 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 tetramethylsilane (TMS). Quantitative UV–vis 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 a 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 **2** and **4** were recorded in linear using positive mode with an average of 100 shots. Spectra for **3** were recorded in linear using reflectron modes with an average of 100 shots.

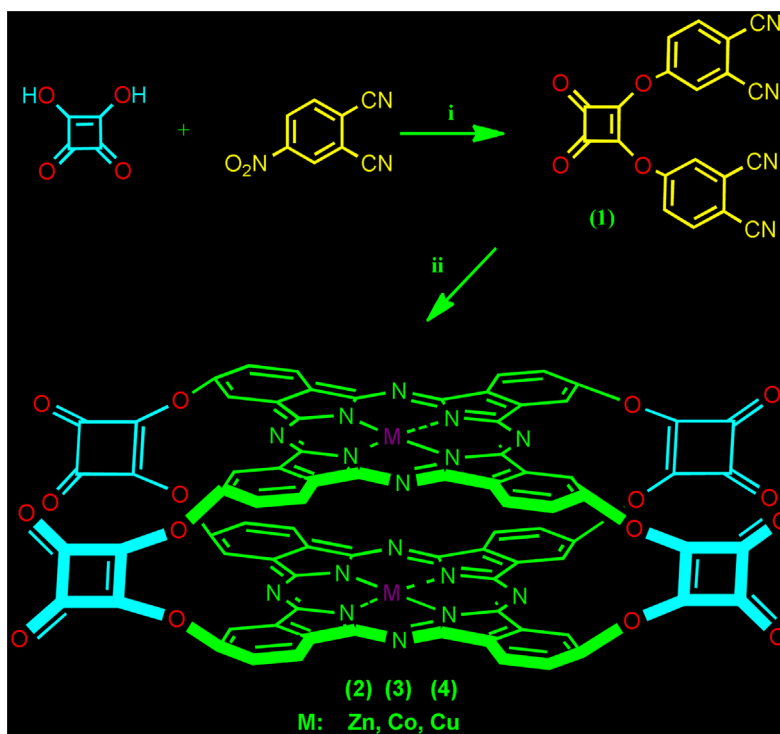
2.2. Synthesis

2.2.1. 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-3cyclobuten-1,2-dione, **2** (1.14 g, 10 mmol) in 15 ml of dry DMF was stirred at 70 °C under Ar. Anhydrous K₂CO₃ (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 with hot water, methanol, and chloroform. This compound is soluble in THF (partially), DMF and DMSO. Yield; 2.90 g (79%), Mp: 262 °C. IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 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-d₆): δ , ppm 7.51–8.25 (m, Ar—H). Anal. Calcd. (%) for C₂₀H₆N₄O₄: C, 65.58; H, 1.65; N, 15.29. Found: C, 66.01; H, 1.80; N, 15.78%.

2.2.2. Synthesis of [2',10',16',24'-tetrakis{4,4'-(3,4-dioxocyclobut-1-ene-1,2-diyl)-bis(oxy)} diphthalocyaninato-dizinc(II)] (**2**)

A well-powdered mixture of compound **1** (0.5 g, 1.36 mmol), at the presence DBU and Zn(OAc)₂·2H₂O (0.124 g, 0.68 mmol) were heated without solvent in an under dry Ar atmosphere sealed glass tube for 15 min at 300 °C. After cooling to room temperature, the crude product was soluble in DMF (5 ml) and precipitated by ice-water mixture. The dark green reaction product was filtered and washed with hot water, ethanol, methanol, chloroform, and acetone. This compound is soluble in DMF and DMSO. Yield: 0.25 g (23%), Mp > 350 °C, IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 3102–3039 (arom. —H); 1771 (C=O); 1720 (C=N); 1588–1482 (Ar—C=C); 1252 cm^{-1} (Ar—O—Ar). ¹H NMR (400 MHz, DMSO-d₆): δ , ppm 7.71–8.31 (m, Ar—H). UV–vis (DMF), λ_{\max} , nm (log ϵ): 675 (4.55), 609 (4.08), 340 (4.42). Anal. Calcd. (%) for C₈₀H₂₄N₁₆O₁₆Zn₂: C, 60.91; H, 1.52; N, 15.78; Zn, 11.79.



Scheme 1. Summary of the synthesis of all compounds. (i) K₂CO₃, Ar, DMF, 70 °C; (ii) (2) Zn(OAc)₂·2H₂O, 300 °C, Ar, without solvent, (3) Co(OAc)₂·4H₂O, 300 °C, Ar, without solvent, (4) Cu(OAc)₂·2H₂O, 300 °C, Ar, without solvent.

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