



Electrochemical properties of metallated porphyrazines possessing isophthaloxybutylsulfanyl substituents: Application in the electrocatalytic oxidation of hydrazine



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ARTICLE INFO

Article history:

Received 23 January 2015

Received in revised form 24 March 2015

Accepted 26 March 2015

Available online 28 March 2015

Keywords:

hydrazine
nanotubes
porphyrazines
sensors
voltammetry

ABSTRACT

The demetallation reaction of sulfanyl magnesium(II) porphyrazine with isophthaloxybutyl substituents, accompanied by remetallation with zinc(II) and cobalt(II) salts, leads to the corresponding zinc(II) and cobalt(II) derivatives in moderate yields. All porphyrazines were analyzed by HPLC and characterized by UV-vis, MS and various NMR techniques (¹H-¹H COSY, ¹H-¹³C HSQC, ¹H-¹³C HMBC). Voltammetric experiments conducted in dichloromethane solution showed that the novel porphyrazine complexes exhibit promising electrochemical properties. For all complexes one electron transfer process was observed in the studied potential range. Cobalt(II) porphyrazine revealed metal-involved redox couple at -0.79 V vs Fc/Fc⁺, as well as peaks derived from ligand reduction/oxidation. Zinc(II) and demetallated porphyrazines showed well-defined macrocycle-based electron transfer processes. A glassy carbon electrode modified by carbon nanotubes/cobalt(II) porphyrazine - composite exhibited great electrocatalytic ability towards the oxidation of hydrazine. A combination of porphyrazine and carbon nanotubes makes it possible to obtain a synergistic effect that increased the rate of hydrazine oxidation. A significant decrease in the overpotential, compared to that obtained through glassy carbon electrode/cobalt(II) porphyrazine or glassy carbon electrode/carbon nanotubes, allows for sensitive determination of hydrazine in neutral conditions (pH 7.4). The novel cobalt(II) porphyrazine macrocycle seems to be a promising material for the design of novel amperometric sensors and electrocatalysts.

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1. Introduction

Porphyrazines (Pzs) are porphyrinoid macrocycles exhibiting interesting physicochemical properties and have numerous potential applications in technology and medicine, especially in the photodynamic therapy of cancer (PDT) and in the photodynamic antimicrobial chemotherapy (PACT) [1,2]. Of special interest are Pzs possessing sulfanyl substituents in their periphery [3,4]. It has been demonstrated that the solubility, aggregation tendency and the level of singlet oxygen generation can be modified through the modification of peripheral substituents.

Some aromatic macrocycles, especially phthalocyanines, porphyrins and porphyrazines, show unique catalytic properties. The ability to undergo fast redox reactions originates from the delocalization of conjugated π electrons across the macrocyclic ring or, more importantly, from redox active metal ions in their center. Thus, among porphyrinoids, particularly those containing redox active metal ions (e.g. Co(III)/Co(II), Fe(III)/Fe(II), Mn(III)/Mn(II)), they are especially useful as electrochemical sensors [5]. Electrodes modified with metalloporphyrinoids act as efficient redox mediators to reduce nitrites [6], oxidate hydrazines [7–9], thiols [10], as well as in the reduction of oxygen and hydrogen peroxide [11,12]. Hydrazine is known as a strong reducing agent that has been widely applied in industry, especially for rocket fuel production, in hydrazine fuel cells, in catalysts and pharmaceuticals [9,13–15]. Hence, the electrooxidation of hydrazine is a very

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important process in the field of electrocatalysis (fuel cells), as well as in electrochemical sensors [8,9,15,16]. However, the direct electrooxidation of hydrazine on conventional bare electrodes suffers due to the slow electron transfer kinetics as a result of a high overpotential. Therefore, it is of constant interest in the development of novel materials to be able to enhance the oxidation current response of hydrazine [8,15]. Carbon nanotubes have been widely used in electrochemistry because of high conductivity and chemical stability, as well as their ability to enhance electrocatalytic properties. In addition, they are known to be excellent supporting materials for the immobilization of organic compounds, enzymes or redox active polymers [17–23]. Such an approach allows obtaining composite materials that exhibit boosted electrochemical properties [19,21].

The catalytic oxidation of hydrazine through the use of various porphyrinoids has been mainly carried out in strong alkaline conditions [24–26]; whereas, the properties of such macrocycles in a neutral pH have been rarely studied [27]. Moreover, Pzs have up until now hardly been studied in the application in electrocatalysis or electrochemical sensors [24].

Lately, we elaborated the novel magnesium(II) porphyrine, possessing isophthaloxybutylsulfanyl substituents, and investigated its photophysical and photochemical properties [28]. In this work, we extended our studies to researching the electrochemical properties of the novel Pz macrocycle and its derivatives. The electrochemical investigation of demetallated Pz and its complexes, with various metal ions in the center, was carried out in an organic solvent by using cyclic voltammetry and differential pulse voltammetry. Our study was focused particularly on the electrocatalytic properties of Pz containing a cobalt(II) ion in its core. For this purpose, multi-walled carbon nanotubes were non-covalently modified through cobalt(II) porphyrine and took advantage of the strong π - π interactions between carbon nanotubes and a porphyrine conjugated system. The electrode material obtained exhibited an enhanced catalytic behavior in hydrazine oxidation in a phosphate buffer (pH 7.4) and this effect was manifested in the lowering of the oxidation potential and the increments of peak current. The electrocatalytic ability was studied with the help of cyclic voltammetry and chronoamperometry.

2. Experimental

2.1. General procedures

All reactions were conducted in oven dried glassware under argon atmosphere using Radleys Heat-On heating system. All solvents were rotary evaporated at or below 50 °C under reduced pressure. Dry flash column chromatography was carried out on Merck silica gel 60, particle size 40–63 μ m. Thin layer chromatography (TLC) was performed on silica gel Merck Kieselgel 60 F₂₅₄ plates and visualized with UV (λ_{\max} 254 or 365 nm). UV-vis spectra were recorded on a Hitachi UV/VIS U-1900 spectrophotometer. ¹H NMR, ¹³C NMR spectra were recorded using Agilent DD2 800 spectrometer operating at frequency 799.905 MHz for ¹H and 201.154 MHz for ¹³C. Chemical shifts (δ) are quoted in parts per million (ppm) and are referred to a residual solvent peak. Coupling constants (*J*) are quoted in Hertz (Hz). The abbreviations s, d, t, h and m refer to singlet, doublet, triplet, hidden and multiplet, respectively. ¹H and ¹³C signals were unambiguously assigned on the basis of ¹H–¹H COSY, ¹H–¹³C HSQC and ¹H–¹³C HMBC spectra. Mass spectra (ES, MALDI TOF) and elementary analysis were carried out by the Advanced Chemical Equipment and Instrumentation Facility at the Faculty of Chemistry, Adam Mickiewicz University in Poznan. HRMS (ESI) spectrum was detected on a Thermo QExactive with the ESI source at the European Center of Bioinformatics and Genomics in Poznan.

2.2. Materials

All solvents and reagents were of reagent-grade quality, purchased from commercial suppliers and used without further purification, unless otherwise stated.

Before use, the purification of multi-walled carbon nanotubes (MWCNTs, 6–9 nm/5 μ m, purity: >95%, Sigma-Aldrich) was carried out through standard procedures, including treatment with hot nitric acid (60 °C for 12 h) [18] followed by etching in hydrofluoric acid, in order to remove amorphous carbon and traces of catalyst, which have been used for their growth. Next, MWCNTs were dispersed in DMF (1 mg mL⁻¹) and ultrasonicated to obtain a stable suspension. For organic electrolyte measurements, compounds **1–4** were dissolved (~0.5 mM) in dry dichloromethane (DCM) with tertbutylammonium salt (TBAP, 0.1 M), which served as a supporting electrolyte. For aqueous experiments, hydrazine solutions were prepared from hydrazine hydrate solution (40%) with double-distilled water and a 0.05 M phosphate buffer (PBS, pH 7.4) was employed as a supporting electrolyte.

2.3. Synthetic procedures

2.3.1. 2,3,7,8,12,13,17,18-Octakis[4-(3,5-dibutoxycarbonylphenoxy)butylthio]porphyrine (2)

2,3,7,8,12,13,17,18-Octakis[4-(3,5-dibutoxycarbonylphenoxy)butylthio]porphyrinato magnesium(II) **1** (56 mg, 0.0166 mmol) was dissolved in trifluoroacetic acid (5 mL) and the solution was stirred at room temperature in the dark for 30 minutes. Next, the reaction mixture was poured into rapidly stirred ice-water (100 mL), neutralized with satd. solution of sodium bicarbonate and then extracted with CH₂Cl₂ (2 \times 50 mL). The organic phases were collected and evaporated to dryness. The crude product was chromatographed using silica gel (dichloromethane:methanol, 50:1, v/v) to give **2** as a dark blue film (35 mg, 63%). *R_f* (hexane:ethyl acetate, 7:2, v/v) 0.55. UV-vis (dichloromethane) λ_{\max} nm (log ϵ): 317 (4.33), 351 (4.25), 504 (3.90), 639 (4.07), 709 (4.22). ¹H NMR (799.905 MHz, pyridine-*d*₅) δ , ppm: 8.21 (s, 8H, C4', ArH), 7.63 (s, 16H, C2'C5', ArH), 4.61 (t, ³*J* = 7 Hz, 16H, SCH₂), 4.27 (t, ³*J* = 7 Hz, 32H, COOCH₂), 4.19 (t, ³*J* = 6 Hz, 16H, CH₂CH₂CH₂CH₂O), 2.45 (m, 16H, SCH₂CH₂CH₂), 2.34 (m, 16H, SCH₂CH₂CH₂), 1.60 (m, 32H, COOCH₂CH₂), 1.34 (m, 32H, COOCH₂CH₂CH₂), 0.87 (t, ³*J* = 7 Hz, 48H, CH₃), -1.55 (s, 2H, pyrrole-NH). ¹³C NMR (201.154 MHz, pyridine-*d*₅) δ 165.7 (C=O), 159.6 (C1', ArC), 141.5 (C2C3, pyrrole), 132.6 (C3'C5', ArC), 122.9 (C4', ArC), 119.8 (C2'C5', ArC), 68.3 (CH₂CH₂CH₂CH₂O), 65.8 (COOCH₂), 35.6 (SCH₂), 31.3 (OCH₂CH₂), 27.9 (SCH₂CH₂), 29.2 (SCH₂CH₂CH₂), 19.9 (CH₂CH₃), 14.3 (CH₃). MS (MALDI): *m/z* 3356 [M+H]⁺.

2.3.2. 2,3,7,8,12,13,17,18-Octakis[4-(3,5-dibutoxycarbonylphenoxy)butylthio]porphyrinato zinc(II) (3)

Compound **2** (18 mg, 0.0054 mmol) and zinc acetate (5 mg, 0.027 mmol) were dissolved in anhydrous DMF (2 mL) and stirred at 70 °C for 24 h. After cooling to room temperature, the solvent was evaporated to a crude residue, which was then chromatographed (hexane:ethyl acetate, 7:3, v/v) to give compound **3** as a blue film (16 mg, 87%). *R_f* (hexane:ethyl acetate, 7:2) = 0.38. UV-vis (dichloromethane) λ_{\max} nm (log ϵ): 317 (4.38), 371 (4.40), 515 (3.78), 673 (4.49). ¹H NMR (799.905 MHz, pyridine-*d*₅) δ , ppm: 8.47 (s, 8H, C4', ArH), 7.82 (s, 16H, C2'C5', ArH), 4.60 (t, ³*J* = 7 Hz, 16H, SCH₂), 4.34 (t, ³*J* = 7 Hz, 32H, COOCH₂), 4.19 (t, ³*J* = 6 Hz, 16H, CH₂CH₂CH₂CH₂O), 2.34 (m, 32H, SCH₂CH₂CH₂), 1.64 (m, 32H, COOCH₂CH₂), 1.36 (m, 32H, CH₂CH₃), 0.87 (t, ³*J* = 7 Hz, 48H, CH₃). ¹³C NMR (201.154 MHz, pyridine-*d*₅) δ 166.0 (C=O), 159.9 (C1', ArC), 158.0 (pyrrole-C1C4), 141.8 (pyrrole-C2C3), 133.0 (C3'C5', ArC), 123.2 (C4', ArC), 120.2 (C2'C5', ArC), 68.7 (CH₂CH₂CH₂CH₂O), 65.8 (COOCH₂), 35.6 (SCH₂), 31.4 (COOCH₂CH₂), 29.3 (SCH₂CH₂CH₂),

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