



# Improved electrocatalytic response toward hydrogen peroxide reduction of sulfanyl porphyrazine/multiwalled carbon nanotube hybrids deposited on glassy carbon electrodes



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## ABSTRACT

We report on the synthesis, physico-chemical properties of magnesium sulfanyl porphyrazine derivatives with peripheral hyperbranched groups and their deposition on the multi-walled carbon nanotube surface. Sulfanyl porphyrazines containing bulky and dendrimeric peripheral benzyloxy units, mers, up to their second generation, were synthesized and characterized using MS, UV–Vis, FT-IR, NMR spectroscopy and HPLC. The morphology of the hybrid nanostructures was researched using SEM and AFM microscopy. Their potential for biomedicine and technology was assessed in an electrochemical study. The electrodes modified with dendrimeric sulfanyl porphyrazine/multiwalled carbon nanotube hybrids were utilized for electrocatalytic determination of hydrogen peroxide, which is an important compound generated in many enzymatic reactions. The strong synergistic effect between two nanostructural components, namely multi-walled carbon nanotubes and dendrimeric porphyrazines was evaluated in the electrochemical study. In the result a significant enhancement of electrochemical properties of the modified electrode was observed. The reversible redox couples derived from porphyrazine ring-based electron transfer were responsible for the improvement of the electrocatalytic response of the modified electrode toward hydrogen peroxide reduction. According to the electrochemical results, multi-walled carbon nanotube - dendrimeric porphyrazine hybrids deposited on the surface of glassy carbon electrode constitute a valuable material for enzyme-free biosensor development.

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## 1. Introduction

Carbon nanotubes (CNT) have gained considerable attention in research due to their unique electronic properties, chemical stability and affinity to biomolecules [1]. It was found that the CNT can promote effective electron transfer reactions. Noteworthy is that the efficiency of electrodes based on CNT is superior to the performance of other conventional electrodes [1,2]. Thus, they have

been often applied in electrochemical sensors and biosensors as the electrode modification material. CNT exhibit enhanced sensitivity toward the determination of many biomolecules including NADH [3], ascorbic acid, uric acid and dopamine [4] as well as hydrogen peroxide [4,5]. Moreover, they can be used as a support for immobilization of different electron transfer mediators onto electrode surfaces able to improve their electrochemical properties. CNT can be easily modified by covalent functionalization [6–8], electropolymerization [9–12] or adsorption [13–15]. Among these techniques, non-covalent adsorption method is an effective way to preserve the sp<sup>2</sup> structures of carbon nanotubes.

Dendrimers as well as nanotubes belong to the larger family of nanostructures. They are highly branched molecules consisting of

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well-defined, repeated multifunctional building blocks. The dendritic core is surrounded by shells containing branches, constituting generations. Dendrimers make up a group of specific polymers which possess a compact shape, a large number of end groups, which are often reactive, and the ability to take up guest molecules between branches. These properties arising from their construction give rise to the possibility of finding applications in many different technological and medical areas [16]. Porphyrinoid-core dendrimers, especially porphyrazine-core dendrimers, deposited on carbon nanotubes are the subject of the electrochemical study presented in this paper. Porphyrinoids themselves are macrocyclic compounds which determine many biochemical processes. Among porphyrinoids an important role is played by natural porphyrins, which are widely distributed in living organisms. Porphyrazines (Pzs) belong to the synthetic analogues of porphyrinoids [17]. Special photochemical and electrochemical properties of porphyrazines proved their potential for diverse technological (catalysts, sensors) and medical applications (photodynamic therapy) [15,18–20]. There has been an increasing interest in the synthesis and research of porphyrinoids, with bulky, hyperbranched and dendrimeric peripheral substituents. It was shown that porphyrins and phthalocyanines with dendrimeric moieties are able to catalyze chemical reactions enantioselectively, and possess interesting physicochemical properties, including reduced aggregation and high levels of singlet oxygen generation [21–27]. The modification of electrode surfaces with different porphyrinoids was considered as a promising approach leading to valuable materials for electrochemistry [28]. This is due to their macrocyclic nature including an extended  $\pi$ -electron system that allowed them to undergo fast redox processes. Among the electrode modifiers reported in the literature, porphyrinoids were considered as powerful electrocatalysts for the electrochemical determinations of many biologically important compounds, such as hydrogen peroxide, ascorbic acid and L-glutathione [8,28,29]. Such electrocatalytic properties were dependent on the central metal ion (e.g. Co, Fe, Mn, Ni) as well as on substituents attached to macrocyclic rings [30]. So far different porphyrinoids have been covalently linked or immobilized on CNT in order to enhance their electrocatalytic ability [31–34]. The  $\pi$ -conjugative structure of multi-walled carbon nanotubes (MWCNT) facilitated its interaction with porphyrinoids during the non-covalent adsorption of the latter. This is due to the strong  $\pi$ - $\pi$  electronic interactions between MWCNT and macrocycle which resulted in highly catalytic, three-dimensional nanostructured wires. In general, electrocatalytic performance using metallated complexes (e.g. Ni, Fe, Mn, Co) are known to involve metal based redox transitions only. On the other hand, an electrocatalytic effect of porphyrinoids resulting from ring-based electroactivity was not so common in the previous studies [35].

In the course of research, we reported the syntheses and discussed the physicochemical properties of sulfanyl Pzs possessing a peripheral system of fluoroalkyl, diether [36], nitroimidazobutyl, and isophthaloxyalkyl substituents [15,19,37–39]. We have found that a glassy carbon electrode modified by carbon nanotubes/sulfanyl cobalt(II) porphyrazine with isophthaloxybutyl substituents – composite, exhibited interesting electrocatalytic ability towards the oxidation of hydrazine, which is of potential value for the design of novel amperometric sensors and electrocatalysts. A combination of porphyrazine and carbon nanotubes caused 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, allowed for sensitive determination of hydrazine in neutral conditions (pH 7.4) [15].

In this study, we report on the synthesis and physico-chemical

characterization of novel magnesium sulfanyl porphyrazine derivatives possessing dendrimeric moieties consisting of benzyloxy units and their deposition on the surface of MWCNT using a simple non-covalent functionalization. The morphology of hybrid nanostructures was researched using SEM and AFM microscopy and they were subjected to electrochemical study. The modified electrodes were also utilized for the electrocatalytic determination of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), which is an important compound generated in many enzymatic reactions. Hydrogen peroxide is relevant in a host defense, oxidative biosynthetic reactions and is a signalling agent in higher organisms [40].

## 2. Experimental

### 2.1. General procedures and materials

All reactions were conducted in oven dried glassware under argon atmosphere. All solvents were rotary evaporated at or below 50 °C under reduced pressure. The reported reaction temperatures refer to external bath temperatures. Dry flash column chromatography was carried out on Merck silica gel 60, particle size 40–63  $\mu\text{m}$  and reverse phase on Fluka  $\text{C}_{18}$  silica gel 90. Thin layer chromatography (TLC) was performed on silica gel Merck Kieselgel 60 F254 plates and visualized with UV ( $\lambda_{\text{max}}$  254 or 365 nm). UV–Vis spectra were recorded on a Hitachi UV/VIS U-1900 spectrophotometer. The FT-IR spectra were recorded using IRAffinity-1 spectrometer (Shimadzu, Japan) with KBr as a blank. The NMR spectra were acquired at 298 K on an Agilent DD2 800 NMR spectrometer operating at resonance frequencies of 799.903 and 201.146 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Chemical shifts ( $\delta$ ) 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 d, s and t refer to doublet, singlet and triplet, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  signals were unambiguously assigned on the basis of  $^1\text{H}$ – $^1\text{H}$  COSY,  $^1\text{H}$ – $^1\text{H}$  NOESY,  $^1\text{H}$ – $^{13}\text{C}$  HSQC and  $^1\text{H}$ – $^{13}\text{C}$  HMBC spectra. Mass spectra (ES, MALDI TOF, HRMS) and combustion analyses were carried out by the Advanced Chemical Equipment and Instrumentation Facility at the Faculty of Chemistry and the Wielkopolska Center for Advanced Technologies at Adam Mickiewicz University in Poznan, and at the European Center of Bioinformatics and Genomics in Poznan. The surface of the cast films of unmodified MWCNTs and  $\text{G}_0/\text{G}_1/\text{G}_2$  dendrimer/MWCNT composites were investigated under a scanning electron microscope (FEI Quanta 250FEG). Atomic force microscopy (AFM) imaging was performed using Agilent 5500 AFM microscope operating in tapping mode with BudgetSensors AllInOne.

All electrolytes, solvents and reagents were of reagent-grade quality, purchased from commercial suppliers and used without further purification, unless otherwise stated. Multi-walled carbon nanotubes (MWCNT, 6–9 nm/5  $\mu\text{m}$ , purity: >95%) were provided by Sigma-Aldrich. Before use, the purification of MWCNT was carried out with standard procedures, including treatment with hot nitric acid (60 °C for 12 h) [1] followed by etching in hydrofluoric acid, in order to remove amorphous carbon and traces of catalyst, which had been used for their growth. Subsequently, MWCNT were dispersed in DMF (1 mg  $\text{mL}^{-1}$ ) and ultrasonicated to obtain a stable suspension. For organic electrolyte measurements, compounds **3a-c** were dissolved in dry dichloromethane with 0.1 M *tert*-butylammonium perchlorate salt (TBAP), which served as a supporting electrolyte. For aqueous experiments, hydrogen peroxide solutions were prepared from 30%  $\text{H}_2\text{O}_2$  solution (Sigma-Aldrich). Phosphate buffer solutions (PBS), Britton-Robinson buffers and 0.1 M perchloric acid were used as electrolytes (all provided by Sigma-Aldrich) with ultrapure water and a 0.05 M phosphate buffer (PBS, pH 7.4) as a supporting electrolyte.

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