



Low symmetric metallophthalocyanine modified electrode via click chemistry for simultaneous detection of heavy metals

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ABSTRACT

Beside different methods and materials used to develop electrochemical sensors, the modification of the electrode using click reaction based on metallophthalocyanine (MPc) compounds are shown to improve the stability and sensitivity of the sensor. This work reported the development of electrochemical sensor for mercury (II), Lead (II), copper (II) and cadmium (II) ions detection based on the synthesized novel low symmetry alkynyl terminated cobalt Phthalocyanine (CoPc) derivative. Differential pulse stripping voltammetry (DPSV) technique was employed for the first time in simultaneous determination of trace levels of the above metal ions using modified glassy carbon electrode (GCE) via click chemistry. Under the optimum experimental conditions, the anodic peak current is proportional to the concentrations of metal ions over a wide range of 0 to 0.1 mM with nanolevel detection limit of 81.94, 327.71, 55.87 and 347.06 nM and the sensitivity of 866.23 ± 5.48 , 215.82 ± 2.16 , 1979.48 ± 11.47 and 204.50 ± 1.10 $\mu\text{A}/\text{mM}$ for Hg(II), Cu(II), Pb(II) and Cd(II), respectively. The selectivity of the clicked-CoPc modified GCE toward Hg(II), Cu(II), Pb(II), Cd(II) present no interference from these metals ions. The fabricated electrochemical sensor exhibited very good electrochemical properties such as good reproducibility, stability, reusability and is suitable for the detection of heavy metal ions in tap water in our laboratory.

1. Introduction

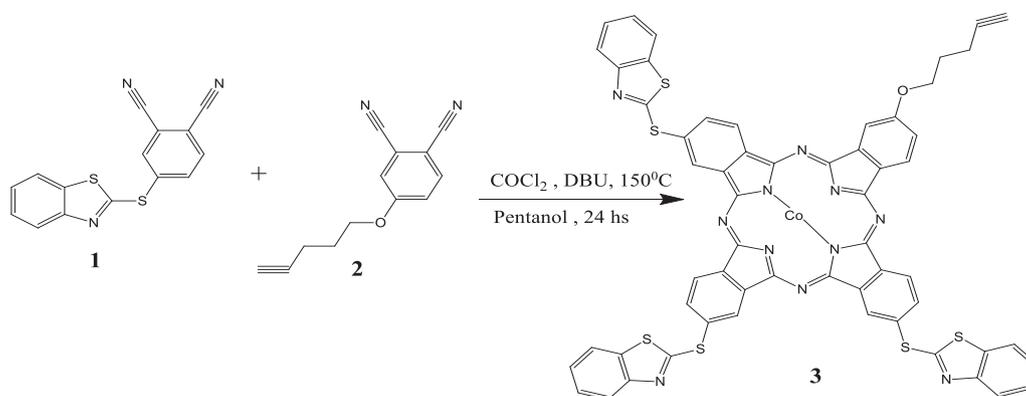
The electrochemical sensors in the past decade represent the most rapidly growing class of chemical sensors for research or industrial applications [1–3]. They have a leading position among the presently available sensors that have reached the commercial stage. They have found a vast range of important applications in the fields of clinical, industrial, environmental and food monitoring. An electrochemical sensor provides low detection limit, high sensitivity, high surface area, good reproducibility, better signal to noise ratio and selective sensing of more than one metal ion [4,5]. These advances include the introduction of modified electrodes, the design of highly selective chemical recognition layers, of molecular devices or sensor arrays, and developments in the areas of microfabrication and flow detectors. The electrochemical method has been reported in literature for the detection of heavy metals but the modification steps of the electrode and the specific techniques employed have been (cyclic voltammetry (CV), open square wave voltammetry (OSWV), differential pulse stripping voltammetry (DPSV) [6–9]. The working electrode can be modified using different methods to enhance the sensitivity, selectivity and reproducibility of the electrochemical sensor. In this work, the modification of the

electrode was carried out via click chemistry which has been reported in literatures [10–16]. The difference between the reported click chemistry for modified electrode and this report is the chemical recognition molecule which is the metallophthalocyanine (MPc) complex and the analyte of interest. The metal phthalocyanines complexes have been used for organophosphorous pesticide detection as well as Quartz Crystal Microbalance (QCM) sensing as presented some literatures [17–19]; and for toxicology [20–25] which is different from this work where we employ a low symmetry metal phthalocyanine for selective detections of heavy metals such as (Hg(II), Cu(II), Pb(II) and Cd(II)). Indeed, these metals can be harmful to human health even in small amounts. Lead and cadmium in the body can cause permanent damage to the central nervous system, the brain, and kidneys and has been implicated in human hypertension [26,27]. Copper is essential substance to human life, but chronic exposure to contaminant drinking water with copper can result in the development of anemia, liver and kidney damage [28,29]. Injection of mercury via drinking water can have harmful effects in the kidneys and brain [30]. Therefore, with this multiple harmful effect of the above metals in human health, there is a need of developing a novel sensitive material for their monitoring.

The synthesis of low symmetric alkynyl substituted cobalt tetrakis

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Scheme 1. Synthetic route for complex 3.

(5-hexyn-oxy) phthalocyanine (CoPc) (complex 3, Scheme 1) employed in this work has not been reported. The complex will be employed for electrode modification using click chemistry [10–12]. The principle of an electro-click reaction is based on two steps starting by grafting the azido-aniline hydrochloride onto bare glassy carbon electrode, followed by clicking the alkyne terminated MPc onto the grafting electrode to form covalent attachment of MPC onto the electrode, which results in very stable thin films onto electrode surfaces for simultaneous detection of Hg(II), Cu(II), Pb(II), Cd(II), As(III). The modification electrode steps were characterized using X-ray photoelectron spectroscopy (XPS) and electrochemical methods.

2. Experimental section

2.1. Instrumentation

UV–vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer in the range 300–800 nm and infra-red spectra were collected on a Bruker Alpha model FT-IR Spectrometer with platinum ATR Elmer 100. Elemental analyses were carried out on a Vario EL III MicroCube CHNS analyzer. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. Magnetic circular dichroism (MCD) spectra were measured using a Chira scan plus spectrodichrometer equipped with a 1 T (Tesla) permanent magnet by using both the parallel and antiparallel fields. The conventions of Piepho and Schatz are used to describe the sign of the MCD signal and the Faraday terms [31]. The electrochemical experiment (electrochemical impedance spectroscopy (EIS)) were performed using Autolab Potentiostat PGSTAT 302 (Eco Chemie, Utrecht, The Netherlands) driven by the general purpose Electrochemical System data processing software (GPES, software version 4.9) while the CV and DPSV were performed using BAS 100B electrochemical work station (LG Fayette). CV, OSWV and DPSV were collected using a conventional three-electrode set-up with a glassy carbon electrode (GCE, 3.00 mm diameter) as a working electrode, platinum wire as a counter electrode and Ag|AgCl (3 M NaCl) as a reference electrode. All experiments were performed at $25 \pm 1^\circ\text{C}$.

2.2. Materials

All reagents were commercially available with analytical grade and were used without further purification. Millipore water was collected from Milli-Q water systems (Millipore corp. Bedford, MA, USA). Sodium hydroxide, hydrochloric acid, acetic acid, and cadmium chloride were purchased from Fluka. Lead chloride were from Riedel-dehaen. Tetrabutylammonium tetrafluoroborate (TBATF₄B), aluminum oxide, ethanol, azido-aniline hydrochloride, sodium nitrite trimethylamine, Bromotris(triphenylphosphine)copper(I) (CuPPh₃)₃Br, potassium carbonate, cobalt chloride, 1-pentanol, 1,8-diazabicyclo[5.4.0]

undec-7-ene (DBU) were obtained from Sigma Aldrich®. Ammonium hydroxide, acetic acid and hydrochloric acid and mercury acetate were purchased from Minema and acetonitrile from Merck. Acetonitrile, Tetrahydrofuran (THF), chloroform, dimethylformamide (DMF), dichloromethane (DCM) and methanol were purchased from SAARC-HEM®. 4-{[4-Benzo(d)thiazol-2-yl]thio} phthalonitrile (1) and 4-(pent-4-yn-1-yloxy)phthalonitrile (2) were synthesized as reported in literature [32,33]. All other solvents were dried by standard methods prior to use.

2.3. Synthesis of tris-[(4-benzo[d]thiazol-2-ylthio)-4-(pent-4-yn-1-yloxy)phthalocyaninato] cobalt (II) (3)

A mixture of 4-{[4-benzo(d)thiazol-2-yl]thio}phthalonitrile (1) (1 g, 3.4 mmol), 4-(pent-4-yn-1-yloxy)phthalonitrile (2) (0.24 g, 1.1 mmol), cobalt chloride (0.3 g, 2.3 mmol), DBU (3 drops) and 1-pentanol (10 mL) was refluxed at 150°C for 24 h under argon atmosphere. On cooling, methanol was added and the precipitated was collected through centrifugation. The product was washed with methanol, ethanol and diethyl ether. The product was further purified by column chromatography using THF and methanol (8:2) as eluent to give a bluish-green solid product. The purified product was dried in enclosed fume hood. Yield: 0.28 g (21%). IR (ATR): ν (cm⁻¹): 3325 (≡C–H), 1623 (C=N/C=C), 745 (C–S). Anal. Calc. for C₅₈H₃₁N₁₁S₆: C, 60.61; H, 2.72; N, 13.41; S, 16.74. Found: C, 60.04; H, 2.69; N, 13.33; S, 16.85. MALDI TOF-MS: Calculated: 1149.28; Found: 1149.39 [M]⁺.

2.4. Electrode preparation and electrochemical measurement

The modification of the electrode was done following the reported method [10–12]. The grafting steps was done by electrodeposition of azido-aniline hydrochloride and scanning from +0.2 to –1 V for 4 cycles in a solution as reported. The electrode was left to click in the presence of (CuPPh₃)₃Br with complex 3 for 24 h. Electrochemical impedance spectroscopy (EIS) was performed in [Fe(CN)₆]⁴⁻ as a redox probe in 1 M of KCl. A potential of 78 mV was applied with perturbation amplitude of 10 mV/s between the frequencies of 10 kHz and 100 Hz.

For electrochemical characterization, 1 mg of the CoPc complex 3 was dissolved in dry DMF containing 0.1 M TBATF₄B as supporting electrolyte. Differential pulse stripping voltammetry (DPSV) was used for the detection of mercury under optimized conditions. Mercury was deposited at the potential of –0.9 V for 180 s by the reduction of Hg(II) in 1 M HCl. The anodic stripping (reoxidation of Hg(0) to Hg(II)) of electrodeposited Hg(0) was performed in the potential range of –0.85 to 0.3 V at the optimized parameters. The simultaneous detection of Cu (II), Cd(II), and Pb(II) was performed at the same experimental condition as in the case of Hg(II). The modification of the electrode was done following the reported method [10–12]. The grafting steps was done by electrodeposition of azido-aniline hydrochloride and scanning from

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