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Spectral and thermal characterization of salophen type Schiff base and its implementation as solid contact electrode for quantitative monitoring of copper(II) ion

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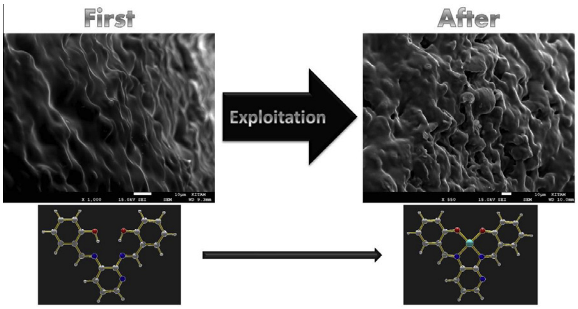
HIGHLIGHTS

- A salophen templated Schiff base have been prepared and fully characterized.
- The compound have been applied as effective ionophore for trace Cu^{2+} detection.
- The obtained electrode has revealed Nernstian response over a wide Cu^{2+} range.
- The ionophore reduces the charge transfer resistance of the electrode.
- The electrode has a very low detection limit for Cu^{2+} in the order 10^{-8} M.

GRAPHICAL ABSTRACT



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ABSTRACT

Salophen templated Schiff base 2,3-bis(salicylaldimino)pyridine (H_2IF) has been synthesized and fully characterized by a series of different spectroscopic methods and thermogravimetric analysis (TGA). It has been also further probed electrochemically and explored as a cation recognition ionophore in the form of a polymeric membrane as selective sensor for quantitative monitoring of Cu^{2+}. Dielectric properties of the membrane have been studied by electrochemical impedance spectroscopy (EIS). The potentiometric results have demonstrated that the sensor exhibits very good selectivity and sensitivity towards Cu^{2+} over a wide variety of cations. The electrode has a linear response to Cu^{2+} with a detection limit of 4.46×10^{-8} and displays a Nernstian slope (29.14 mV/decade) between pH 3.0 and 6.0 with a fast response time less than 10 s. The solid contact electrodes have been exploited over five mounts period with good reproducibility. The analytical availability of the proposed electrode has been evaluated by applying in the determination of Cu^{2+} ions in water samples. The structural features and complexation of ionophore with Cu^{2+} have been monitored by UV–Vis spectroscopy and spectral findings have been further supported by DFT and TD-DFT calculations.

Introduction

Salens/Salophens regarded by coordination chemists as privileged ligand class with their [N,N,O,O] tetradentated donor sites and corresponding metal complexes of these strong chelators have been extensively studied for many fruitful applications such as building blocks in supramolecular and materials chemistry, metal chelating agents, unique heterogeneous and homogenous catalysts, antimicrobial, antitumor, spectrophotometric and fluorimetric agents, optical and electrochemical sensors, efficient fluorescence emitters and anion recognizing receptors, the

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chemistry of which is still infant. Such a versatile implementations of Salens/Salophens arise from their large diversities, unique electronic properties, and efficient potencies to participate strong Lewis acid/base and/or columbic interactions with almost all metal species [1–12]. Based on the strength of their diverse and easy accessibilities, an increasing challenge by synthetic chemists has been continuing to prepare Schiff base ligands containing various donor atoms such as nitrogen, oxygen and sulfur (NOS). The presence of both hard/borderline oxygen/nitrogen and soft sulfur donor atoms enhances the coordination of these ligands to wide range of transition metal ions by yielding stable metal complexes [13,14]. Adding to above mentioned applications of these strong chelators, they also act as ion carriers in the polymeric membranes and produce remarkable selectivity, sensitivity and stability for a specific ion [15,16]. Potentiometric ion selective sensors comprising Schiff bases as electro-active ingredient have been reported to exhibit excellent selectivity and sensitivity for specific metal ions [15,17,18]. Peculiarly, Salen/Salophen based Schiff bases incorporated as neutral carriers have been also reported as ion selective electrodes for determination of diverse heavy metal cations [19–27]. The development of polymeric membrane ion-selective electrodes with internal solid contact (SC ISEs) has received widespread attention during the recent years because of their special advantages including simple construction, small size, low cost of production, and mechanical stability. They can have various shapes and sizes as well as can work in any position, color and turbid solutions [28]. The design of new electrodes for specific analytical applications is a subject of continuous interest. On this context, the versatile applications of aforementioned Ligand classes with their flexible topologies have necessitated an ongoing research on these compounds and their derivatives.

Therefore, the aim of the present work, in continuation of our previous report [29], is to characterize in more detail a neutral salophen-Schiff base ligand on the basis of spectroscopic (UV,NMR, IR, ESI-MS) and thermal (TGA) techniques. The cation recognition characteristics of H_2IF were evaluated by its application as the potentiometric sensor of Cu^{2+}. The Schiff base was used to construct solid contact Cu^{2+} selective sensor for quantitative detection and dielectric performance of the membrane has been studied by EIS.

Experimental

Synthesis of H_2IF

The ionophore H_2IF (IF: dianion of neutral H_2IF) was prepared according to procedure which was applied in our previous study using the same ratios of reactants [29]. Yield: 85%. Anal. Calc.C, 71.91; H, 4.76; N, 13.24. Found: C, 71.92; H, 4.82; N 13.67. IR (KBr, cm^{-1}): 3476 $\nu as(OH)$; 3043 $\nu_{ar}(CH)$; 1615–1606 $\nu(C{=}N)$; 1553 $\nu(C{=}C)$ (see IR spectral data in Supporting information SI5).

Preparation of solid contact copper-selective electrodes

The solid contact electrode was prepared as described in our previous work [29]. Conductive solid contact was prepared as follows: a mixture of conductive material consisting of 50% (w/w) graphite, 35% (w/w) epoxy, and 15% (w/w) hardener was prepared by mixing in sufficient THF. When appropriate viscosity were attained, a shielded copper wire with the length of 5 cm and radius of 0.5 mm was dipped into this mixture a few times to obtain a solid contact with coating thickness of about 0.2 mm.

The coating membrane cocktails of the electrodes were prepared by dissolving sensing material (salophen), solvent mediators (dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (NPOE), dioctyl sebacate (DOS), benzyl acetate (BA), anion excluders (KTpClTB (potassiumtetrakis (p-chlorophenyl) borate KTpClTB and sodium tetraphenyl borate (NaTPB) and PVC in 4 ml of THF. The surface of the conductive material covered with this membrane was dipped into the membrane cocktail 4–5 times to obtain a membrane thickness of about 0.2 mm. Then the membrane coated electrode was left to be dried at laboratory conditions overnight. Finally, the dried membrane electrode was conditioned for at least 4 h in 10^{-6} M $Cu(NO_3)_2$ solution to saturate PVC membrane in the primary ions before use.

For each membrane composition, four identical electrodes were prepared and subjected to the same studies. The electrodes were stored in the laboratory conditions when not in use. Before individual measurement process, the electrodes were reconditioned at least 10 min in 10^{-6} M $Cu(NO_3)_2$ solution.

Reagents and solutions

The solutions of metal salts were prepared with the relevant cations using freshly double distilled water. 10^{-1} M stock solutions for each cation were prepared. The dilute solutions (10^{-2} to 10^{-7} M) were prepared by gradual dilution of the cation stock solutions. For the study of pH effect, the solutions (pH 2.0–8.0) which have fixed Cu^{2+} concentrations of 10^{-2} M and 10^{-3} M were prepared. Nitric acid (10^{-1} M) and sodium hydroxide (10^{-1} M) solutions were used for pH adjustment.

Materials and measurements

ESI-MS spectrum was recorded in methanol on an AB SCIEX QTRAP® 5500 LC/MS/MS SYSTEM Mass spectrometer (USA). The samples were dissolved in hypergrade methanol stirring in a Banderin Sonorex ultrasonic bath and infusion (continuous signal) method with a flow rate of 5–20 μm/min was used for mass scanning. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer (USA). IR spectra were recorded on a Bruker Vertex-80V spectrometer (GERMANY) in the range 4000–400 cm^{-1} using KBr pellets. Thermal analysis measurement was conducted with Perkin Elmer Pyris 1 TGA thermal analyser (USA), within 50–1000 °C temperature range, in static air atmosphere at a heating rate of 10 °C/min. ^1H-NMR measurements were conducted on a Bruker AVANCE III 400 MHz NMR spectrometer (GERMANY) using $CDCl_3$ solution. The absorbances were measured on a Thermo Array Evolution UV–Vis spectrophotometer (USA) controlled by Viscon collect software. The measurement of the electromotive force (EMF) of the system, copper electrode – reference electrode saturated calomel electrode (SCE) (Gamry), was carried out at room temperature in a solution stirred with a mechanical stirrer by means of laboratory-made high-input impedance eight channels potentiometric measurement system connected to a personal computer. The system has a home-made software program. The pH of the buffer solutions was monitored by using a glass pH electrode (Schott) connected to a Jenway 3040 model Ion Analyser.

Electrochemical impedance spectroscopy (EIS)

EIS measurements were performed in 0.001 M $Cu(NO_3)_2$ by using a Gamry (reference 600) electrochemical analyzer controlled by FRA software, version 4.9 (Eco Chemie, Utrecht, Netherlands) with a conventional three-electrode system, where the studied electrode was connected as the working electrode. The reference electrode was Ag/AgCl (Gamry), and the auxiliary electrode was a platinum wire. The impedance spectra were recorded at open circuit potential with amplitude 0.1 V and in the frequency range 10 Hz–100 kHz.