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Development and characterization of a copper ion-selective optical sensor based on a novel calix[4]dicyano-diimidazole thin film

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HIGHLIGHTS

- We report optical sensor based on calix[4]dicyano-diimidazole membrane.
- We introduce the proposed optode for sensitive and selective determination of Cu^{2+}.
- The dynamic range, reproducibility, ion selectivity and life lime were discussed.

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ABSTRACT

A novel optical sensor for sensitive and selective determination of copper ions in aqueous solution based on a novel calix[4]dicyano-diimidazole ionophore was prepared. The newly synthesized calix[4]dicyano-diimidazole exhibited obvious absorbance enhancement at 284 nm in the presence of copper ions. At pH 6.8, the measuring range of the optode membrane for Cu^{2+} ions was from 1.0×10^{-8} to 1.0×10^{-4} M with a detection limit of 7.0×10^{-9} M. Furthermore, the response time of the proposed optical device was within 10 min. With the optimum condition described, the optical sensor revealed good selectivity toward Cu^{2+} ions in comparison with common coexisting cations (Hg^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}). Finally, the reproducibility, regeneration, reversibility and repeatability of this optical sensor were discussed.

1. Introduction

Among the essential heavy metals, the abundance of copper ranks the third in human body. It participates in many biological processes, such as haemoglobin synthesis, development of connective tissue, normal functions of the central nervous system, and oxidative phosphorylation [1–3]. Nevertheless, copper of high concentration is highly toxic to some organisms such as many bacteria and viruses [4]. Copper is also found to be harmful to human at high concentration and has been suspected to cause the damage of infant liver in recent years. Due to the toxicity of copper, the World Health Organization (WHO) suggested the Cu(II) concentration in drinking water must not exceed 2 mg L^{-1} [5,6]. The European Water Quality Directive (EWQD) also suggested that Cu(II) concentration in drinking water must not go over 2 mg L^{-1} [7]. Thus, due to the clear need for determining of Cu^{2+} ions in many industrial, environmental medicinal and food samples, recently there are a lot of techniques being developed for Cu sensing. Many sensitive techniques such as atomic absorption spectrometry (AAS) [8], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [9], ion-selective electrode (ISE) [10,11], anodic stripping voltammetry (ASV) [12,13], fluorescence spectroscopy [14,15] and spectrophotometry [16,17] have been widely applied to the determination of copper. Among these methods, spectrophotometry offers significant advantages due to its nondestructive character, high sensitivity and specificity.

Optical sensors are suited for the analysis of copper as they offer the selectivity and sensitivity necessary for environmental monitoring. The major characteristic points of optodes are small instrumentation, easy operation and low cost. From a practical viewpoint, these points are necessary in order to use optodes in a wide variety of fields and measure many samples. Some optical sensors have been constructed and used for determination of Cu(II) using various chromogenic reagents over the last decade [18–24].

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The summarized data include the reagents; working range and/or limit of detection (LOD) of copper sensors are shown in Table 1.

Calixarenes ligands are frequently used as ionophores in construction of membrane sensors because of their highly selective recognition and complexation with metal cations and organic molecules [25,26]. The availability of chromogenic calixarene molecules which in solution phase experiments exhibited a variation in their absorption or fluorescent spectra due to interactions with metal cations, initiated research work to utilize this type of chromogenic ligands in optical sensors.

Earlier researches in our laboratory are interested to study optical sensors based on chromogenic calix[4]arene ionophores. R. Ebdelli et al. [27] have shown that the tetrakis-(phenylazo) calix[4]arene amide derivative, exhibited good sensitivity toward Hg^{2+}, Ni^{2+} and Eu^{3+} ions. M. Echabaane et al. [28,29] have developed optical chemical sensors based on 5,17-bis(4 nitrophenylazo)-26,28-dihydroxy-25,27-di(ethoxycarbonylmethoxy)-calix[4]arene and 5,17 bis(phenylazo)-26,28 bis{[(ethoxycarbonyl)methylcarbamoyl]methoxy}-25,27-di(ethoxycarbonylmethoxy)-calix[4]arene for the determination of Eu^{3+} and Al^{3+} ions, respectively.

In the present study, we introduce a novel optode for sensitive and selective determination of Cu^{2+}, based on a recently synthesized calix[4]dicyano-diimidazole (Fig. 1) as the sensing membrane by coating the new chromogenic reagent on glass plate substrate. The proposed optical sensor shows a significant absorbance signal change on exposure to an aqueous solution containing Cu^{2+} ion. The selectivity, response time, reproducibility, reversibility and repeatability of the optode membrane were studied. As shown on Table 1, this optode has a lower detection limit and a wider linear range relative to other reported optode for copper ions.

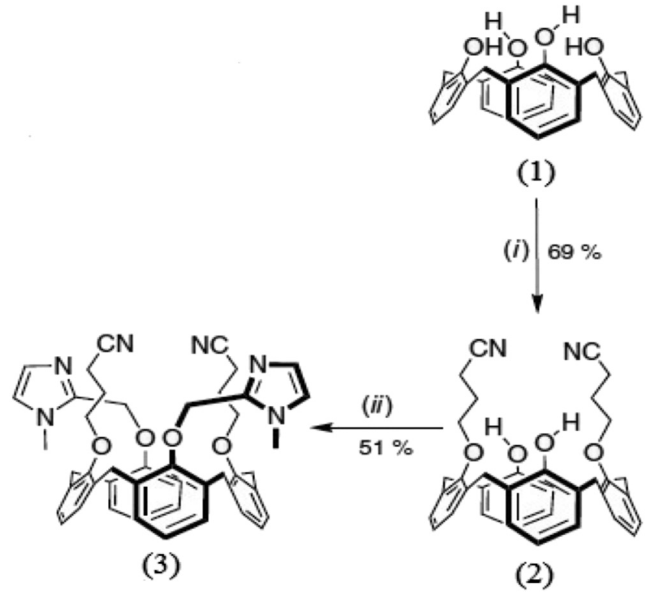

Fig. 1. Reaction sequence for the synthesis of the calix[4]dicyano diimidazole (compound 3): (i) CH_3CN/K_2CO_3, $Br(CH_2)_3CN$; (ii) NaH, THF, 2-chloromethyl-N-methylimidazole.

2. Experimental

2.1. Apparatus

Spectrophotometry measurements were recorded on a DR5000 HACH LANGE UV/vis Spectrophotometer with 3-cm quartz cells, within the range between 200 and 900 nm. The pH values were determined with a HANNA pH meter (model 8519N) using a combined glass electrode. Optical measurements were carried out at room temperature.

2.2. Synthesis of the calix[4]dicyano-diimidazole as ionophore

The new calix[4]dicyano-diimidazole ligand was synthesized according to an efficient two step sequence starting from the de-tert-butylated calix[4]arene (1). Following a literature procedure [30], the regioselective dialkylation of (1) with an excess of 4-bromobutyronitrile in the presence of K_2CO_3 afforded the dicyanocalixarene (2) in 69% yield. Alkylation of the two remaining hydroxy positions using 2-chloromethyl-N-methylimidazole with NaH in THF led to the targeted ligand calix[4]dicyano-diimidazole (3) in 51% yield. The white-colored product was soluble in chloride solvents such as chloroform ($CHCl_3$). The structural formula and detailed complexation investigations of the prepared calix[4] arene derivative were reported by NMR, Infra-red, and MS analyses [31]. Fig. 1 displays the synthesis of the novel calix[4]dicyano-diimidazole.

2.3. Chemicals and solutions

Analytical reagent grade $CuSO_4$, $Hg(NO_3)_2$+ $2H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2$, $NiCl_2$+$6H_2O$ and $ZnSO_4$+$7H_2O$ were used. Distilled water was used for preparation of the solutions. All buffer solutions were prepared from Tris/HCl (0.1 M), ammonium acetate/acetic acid (0.1 M). The pH is adjusting to the desired value. A stock solution, 0.1 M Cu(II) was prepared by dissolving 0.159 g of $CuSO_4$ in a 10 ml volumetric flask. Dilute solutions were freshly prepared by serial dilution of the stock Cu(II) solution. The membrane solution was prepared by dissolving 4 mg of calix[4]dicyano-diimidazole in 1 ml $CHCl_3$.

2.4. Preparation of optode film

The glass plate substrates were successively cleaned for 15 min in acetone, methanol and isopropyl alcohol in an ultrasonic bath and finally dried by a nitrogen gas flow. Cleaned substrates were

Table 1
Some reported optical sensors for the determination of Cu(II).

Reagents	Linear dynamic range (M)	Detection limit (M)	Measured signal	Reference
N,N′-bis (salycilidene)-1,2-phenylenediamine (salophen)	5.01×10^{-8} to 6.32×10^{-4}	4.7×10^{-8}	Absorbance	[18]
1-hydroxy-2-(prop-2′-enyl)-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ)	1.0×10^{-6} to 1.0×10^{-2}	–	Fluorescence	[19]
Carboxylic Acid-functionalized Tris(2,2′-bipyridine)-ruthenium(II) Complex	5.0×10^{-8} to 1.0×10^{-4}	4.2×10^{-8}	Fluorescence	[20]
1-hydroxy-3,4-dimethyl-9-H-thioxanthen-9-one (HDTO)	1.6×10^{-7} to 1.3×10^{-2}	4×10^{-7}	Absorbance	[21]
1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone (PPDOT)	7.5×10^{-6} to 2.0×10^{-4}	8.0×10^{-7}	Absorbance	[22]
2-(2-Aminoethyl) pyridine-tricarbocyanine	4.8×10^{-7} to 1.6×10^{-4}	9.3×10^{-8}	Fluorescence	[23]
lipophilized nitroso-r (NRS)	7.87×10^{-5} to 1.57×10^{-3}	2.22×10^{-5}	Reflectance	[24]
calix[4]dicyano-diimidazole	1.0×10^{-8} to 1.0×10^{-4}	7.0×10^{-9}	Absorbance	This work