

Amine-derivatized calix[4]arenes for sensitive extraction of cupric ion and formation of amine radical cation



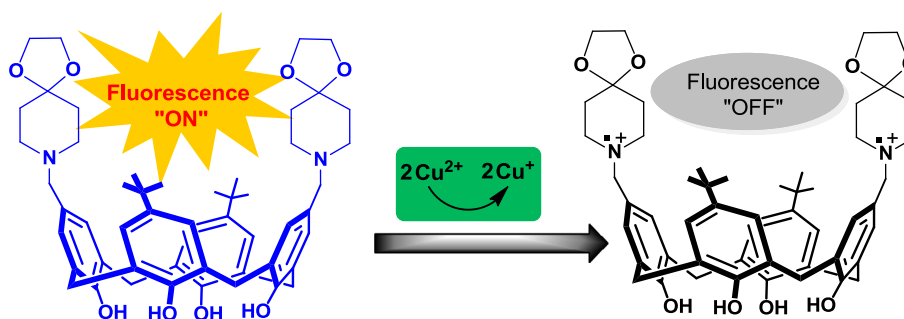
Begum Tabakci*, Aydan Yilmaz

Selçuk University, Department of Chemistry, 42075 Konya, Turkey

HIGHLIGHTS

- New calix[4]arene amine derivatives were easily synthesized via Mannich procedure.
- New calix[4]arene amine derivatives were efficient and selective receptors for Cu^{2+} cation.
- The sensitive extraction of cupric ions and formation of calix[4]arene amine radical cation took place concurrently.
- It was developed new “naked eye” chemosensor and new “turn-off” probe for cupric ions.
- The generation and study of amine radical cations with calixarene derivatives has been documented for the first time.

GRAPHICAL ABSTRACT



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ABSTRACT

We report herein some calix[4]arene amine (C[4]A) derivatives, which are the copper(II)-induced fluorescence “turn-off” and “naked eye” chemosensors and the agents for the formation of amine radical intermediates. In this way, concurrently, the sensitive extraction of cupric ions and the formation of amine radical cations with calixarenes have been documented for the first time. These data were confirmed by using some experimental studies such as UV–visible, fluorescence, electron spin resonance, and cyclic voltammetric.

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Introduction

In recent years, the development of selective and sensitive chemosensors capable of reporting transition metal ions has attracted considerable attention [1,2]. A great effort has been devoted to the development of selective chemosensors due to the

biological and environmental importance of Cu^{2+} ion [3–12]. It is the third adequate element following iron and zinc and plays crucial roles in many fundamental physiological processes in organisms. It is well known that it serves as a catalytic cofactor for various metalloenzymes including superoxide dismutase, cytochrome c oxidase, and tyrosinase [13], whereas unregulated overloading of copper can lead to severe neurodegenerative diseases such as Alzheimer's [14] or Parkinson's diseases [15]. Cu^{2+} is also suspected to cause infant liver damage in recent years

* Corresponding author. Tel.: +90 332 2233880; fax: +90 332 2412499.

E-mail address: btabakci@selcuk.edu.tr (B. Tabakci).

[16,17]. Thus, the highly selective, sensitive, and rapid recognition of Cu^{2+} by chemosensors in aqueous media is still imperative.

Amine radical cations, important intermediates in a large number of single electron transfer (ET) reactions [18–20], occur by the one electron oxidation of amines and are concerned with the synthesis of amino acids, alkaloids, and several other nitrogen-containing compounds of biological and pharmaceutical importance [21,22]. They are important materials in several technological applications such as imaging [23] and photopolymerization [24]. Therefore, generation and reactivity studies of radical cations are very important.

Calixarenes [25–28] are metacyclophanes composed of phenolic and methylene units and versatile ionophores, which provide a platform for attachment of convergent binding groups to create host molecules primarily for attraction of simple cations, anions, and small molecules [29–35]. They have been widely used as an ideal platform for the development of fluorescence chemosensors for not only alkali and alkaline-earth metal ions but also transition metal ions including Cu^{2+} [36–41]. Hence, in the light of these expressions, it was considered that the sensitive copper extraction and the formation of amine radical cation were accomplished by using the calixarenes at the same time. To investigate this assumption, various calix[4]arene amine (C[4]A) derivatives were synthesized (Scheme 1), due to their extraction activities for heavy metal cations [42–45], and their cation-sensing properties for Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+} were examined.

Experimental section

General

Melting points were determined using an Electrothermal 9100 apparatus in a sealed capillary and were uncorrected. NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl_3 with TMS as the internal standard. IR spectra were obtained on a PerkinElmer Spectrum 100 IR spectrometer. Metal contents of samples in extraction studies were determined by Perkin Elmer ICP-MS, Elan DRC-e. UV–visible spectra were measured with a Perkin Elmer Lambda 25 spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS 55 spectrometer. ESR measurements were carried out at room temperature with X-band ESR spectrometer (JES-FA300, JEOL). Cyclic voltammetry was performed with a CHI 600C electrochemical workstation in a conventional three-electrode electrochemical cell. Working electrode was a bare glassy carbon (GC) disk (BAS Model MF-2012) with a geometric area of 0.027 cm^2 . A platinum wire and $\text{Ag}/\text{AgCl}/\text{KCl}$ (sat.) electrode were used as the auxiliary and the reference electrodes, respectively. Elemental analyses were performed using a LECO CHNS-932 analyzer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). The chromatographic separations were performed on a Merck Silica Gel 60 (230–400 mesh). All reactions were conducted in nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Sigma–Aldrich and used without further purification. The commercial grade solvents were distilled and stored over molecular sieves. The drying agent employed was anhydrous sodium sulfate. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

Synthesis of calix[4]arene amines

Compounds 1–5 were synthesized by previously published procedures [46], while the rest of the compounds 6 and 7 are reported

in the present study according to following Mannich procedure. To a solution of 4 (1.50 g; 4.6 mmol) in a mixture of 70 mL of THF:DMF (5:2) were added acetic acid (2.66 mL), respective amine (11.5 mmol; 1,4-dioxo-8-azaspiro-[4.5]decane or piperidine (5.1 mmol for 6)), and aqueous formaldehyde (0.31 mL, 37%), and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in deionized water (75 mL). The aqueous solution was extracted twice with diethyl ether (50 mL) and then neutralized with aqueous K_2CO_3 solution (10%). The precipitate that formed was removed by suction filtration. The products were dried in vacuo and recrystallized from chloroform/methanol to give pure 5, 6, and 7.

5,17-Di-tert-butyl-11-H-23-(piperidino)methyl-25,26,27,28-tetrahydroxycalix[4]arene (6)

This compound was prepared with piperidine (5.10 mmol) as described in general procedure above. Yield: 62%, mp: 147 °C. ^1H NMR (CDCl_3): δ 1.28 (s, 18H, Bu^t), 1.42 (brs, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.57 (p, $J = 5.4 \text{ Hz}$, 4H, $\text{CH}_2\text{CH}_2\text{N}$), 2.33 (bs, 4H, CH_2NCH_2), 3.27 (s, 2H, ArCH_2N), 3.52 (d, $J = 13.1 \text{ Hz}$, 4H, ArCH_2Ar), 4.26 (t, $J = 13.1 \text{ Hz}$, 4H, ArCH_2Ar), 6.72 (t, $J = 7.4 \text{ Hz}$, 1H, ArH), 6.95–7.1 (m, 8H, ArH), 8.53 (bs, 4H, OH). ^{13}C NMR (CDCl_3): δ 148.83, 146.71, 144.52, 129.79, 128.93, 128.48, 128.07, 127.62, 127.41, 125.95, 125.78, 122.27, 63.32, 54.44, 34.07, 32.14, 32.21, 31.48, 25.82, 24.29. FAB-MS m/z : 656.69 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd. for $\text{C}_{42}\text{H}_{51}\text{NO}_4$ (633.86): C, 79.58; H, 8.11; N, 2.21. Found: C, 79.83; H, 7.95; N, 2.13.

5,17-Di-tert-butyl-11,23-(piperidino)methyl-25,26,27,28-tetrahydroxycalix[4]arene (7)

This compound was prepared with piperidine (11.5 mmol) as described in general procedure above. Yield: 68%, mp: 230 °C. ^1H NMR (CDCl_3): δ 1.23 (s, 18H, Bu^t), 1.40 (brs, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.54 (p, $J = 5.6 \text{ Hz}$, 8H, $\text{CH}_2\text{CH}_2\text{N}$), 2.29 (bs, 8H, CH_2NCH_2), 3.23 (s, 4H, ArCH_2N), 3.50 (d, $J = 13.4 \text{ Hz}$, 4H, ArCH_2Ar), 4.23 (d, $J = 13.4 \text{ Hz}$, 4H, ArCH_2Ar), 6.96 (s, 4H, ArH), 7.05 (s, 4H, ArH). FAB-MS m/z : 753.86 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{N}_2\text{O}_4$ (731.02): C, 78.86; H, 8.55; N, 3.83. Found: C, 79.11; H, 8.35; N, 3.77.

Liquid–liquid extraction studies

The extraction experiments of 5–7 were performed following Pedersen's procedure [47]. An aqueous solution of metal nitrate (10 mL of a $2.5 \times 10^{-5} \text{ M}$) and calixarene derivative (10 mL of $1.0 \times 10^{-3} \text{ M}$) in dichloromethane was shaken vigorously in a stoppered glass tube with a mechanical shaker for 2 min and then magnetically stirred in a thermostated water bath at 25 °C for 1 h and finally left standing for an additional 30 min. Blank experiments showed that no metal extraction occurred in the absence of C[4]A derivatives. The concentration of the metal ion remaining in the aqueous phase after the extraction was then determined by ICP-AES. The percentages of extraction (Ex %) were determined from Eq. (1).

$$\text{Ex}\% = ([M]_{\text{blank}} - [M]_{\text{final}}) * 100 / [M]_{\text{blank}} \quad (1)$$

where $[M]_{\text{blank}}$ and $[M]_{\text{final}}$ represent the metal concentration in the aqueous phase extracted with pure dichloromethane and with the dichloromethane solutions containing ligands, respectively.

UV–visible and fluorescence studies

The stock solutions of ligands 5–7 and metal perchlorates (Attention!!! Perchlorate salts are potentially explosive) were prepared in acetonitrile (ACN). The concentrations of the solutions

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