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Highly selective chromogenic ionophores for the recognition of chromium(III) based on a water-soluble azocalixarene derivative

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Abstract

A new water-soluble chromium-selective chromogenic azocalix[4]arene had been synthesized from diazo coupling reaction between calix[4]arene and diazonium salts, and characterized by ^{1}H NMR, IR,UV and element analysis. It possesses an absorbance maximum at 365 nm in buffered aqueous environment, but addition of chromium(III) ion induced a weak blue shift to 350 nm and a new absorption peak at 520 nm (bathochromic shift of 155 nm), exhibited an isosbestic point at 470 nm. It is more noticeable that the absorbance at 520 nm increases along with the augment of the concentration of chromium(III) ion. Based on this, a simple and selective spectrophotometric method was developed for the determination of chromium(III), in the range of 9.35×10^{-4} to 4.45×10^{-3} mol L^{-1} of chromium(III) the linear regression equation was determined to be: absorbance (A) = 0.001 × C (10^{-4} mol L^{-1} chromium(III)) + 0.2379, r = 0.998, n = 6.

Keywords: Chromium; Azocalix[4]arene; Chromogenic; Spectrophotometry

1. Introduction

There has been much recent interest in the design of new stimuli responsive host systems. Of these, the developments of chromogenic or fluorogenic ionophores have been a very active research area in supramolecular chemistry, since these can be applied to many useful and important chemical sensor technologies. Calixarenes, which are accessible by the base-catalyzed condensation of *para*-substitued phenols with formaldehyde, are ideal frameworks for the development of chromogenic ionophores in the molecular recognition of ionic species of chemical and biological interest since the incorporation of a suitable sensory group into the calixarene result in a tailored chromogenic receptor. A variety of compounds based upon calixarene having nitrophenylazophenol [1–4], nitrophenol [5], indoaniline [6], indophenol [7], and azophenol [8] functional groups have been successfully designed and exhibit a pronounced chromogenic behavior towards Na$^+$, K$^+$, Cs$^+$, Ca^{2+}, UO$_2$$^{2+}$, and even chiral amines. Shinkai et al. had synthesized calix[4]arene with a 4-(4-nitrophenyl)azophenol unit and three ethyl ester residues on the lower rim and observed the lithium sensitivity of the ionophore. Toth et al. also reported the sodium selectivity of related azophenol derivatives [9]. However, there has been no reports on calixarene-based selective chromoionophores for detecting chromium(III) ion up to now.

Chromium(III) is one of the most important component of endocrine gland in vivo, which can catalyze the process the metabolism of glucose and cholesterin. Lack of chromium(III) will results in turbulence in the metabolism of glucose and cholesterin, even atheroma. On the other hand, over much chromium(III) in nature environment will endanger soil, jeopardize plants and humankind. So development of a simple, sensitive and reliable method for the determination of chromium(III) is essential, it is even more interesting and

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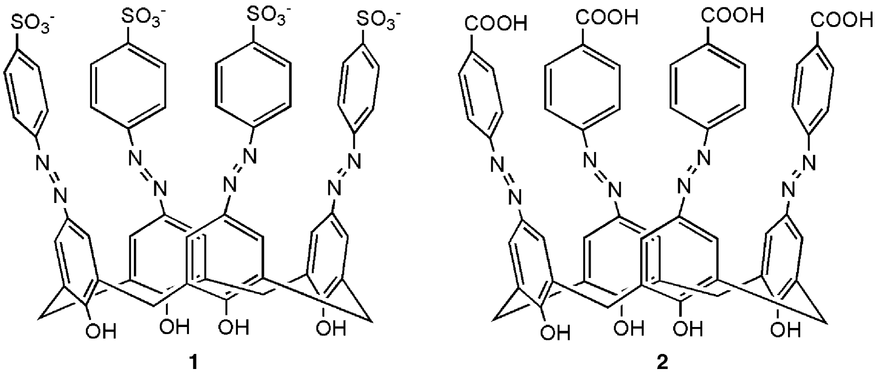

Scheme 1.

significant to develop a new type of calixarene-based chromogenic reagent for selective detection of chromium(III).

Generally, the most chromogenic reagents based on the supramolecular calixarene were prepared by attaching a chromogenic moiety for the optical reading-out to the platform of calixarene, their ability to recognize and discriminate metal ions is one of the most remarkable features in previous reports, which makes them suitable as specific receptors. Similarly the target reagents 5, 11,17,23-tetrakis[(*p*-sulfophenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (**1**) and 5,11,17,23-tetrakis[(*p*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (**2**) (Scheme 1) in this paper were synthesized through a diazo-coupling reaction between the calix[4]arene and diazonium salts, and they both displayed excellent chromogenic behavior towards chromium(III). This motivated us to study it deeply, the following experiment did validate that the two reagents both exhibit good selectivity for chromium(III), thereinto the reagent **1** is more excellent.

2. Experimental

2.1. Reagents and materials

All chemicals and solvents used were of analytical grade and used without further purification unless otherwise mentioned. Double distilled and degasified water was used throughout.

2.2. Apparatus

^{1}H NMR spectra were measured on Avance 500 Bruker spectrometer in D_2O with tetramethylsilane as the internal standard. Infrared spectra were taken in KBr pellets on Nicolet 170X FT-IR spectrophotometer in 400–4000 cm^{-1} region. UV spectra were measured with Cintra 10e UV spectrophotometer (GBC, Australia) in aqueous or DMF solution. C, H and N were determined using a Perkin-Elmer 240 C elemental analyzer. Uncorrected melting point were measured on an melting point apparatus (Beijing, China). The pH values were determined at room temperature with a digital pHS-3C meter (Shanghai, China) calibrated to standard buffer solutions of pH 6.96 and 4.00.

2.3. Synthesis of 5,11,17,23-tetrakis[(p-sulfophenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (1) and 5,11,17,23-tetrakis[(p-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (2)

The synthesis of *p-tert*-butylcalix[4]arene was performed according to the method available described in literature [10]. Calix[4]arene was prepared by debutylation of *p-tert*-butylcalix[4]arene [11]. Reagent **2** was synthesized referring to the literature [12].

Reagent **1** was synthesized as follows (Scheme 2): to a 10 mL solution of aqueous NaOH (5%), 1.9 g sulfanilic acid crystal was added while constantly stirring. After the mixture was cooled to 5 °C in ice bath, a solution of 0.8 g $NaNO_2$ in water was added, then acidified by diluted aqueous HCl solution. After half-an-hour stirring, a solution of diazo salt was obtained. A little urea (ca. 0.2 g) was then added and the solution was stirred for further 10 min.

Into a cold solution of 1.0 g (2.36 mmol) calix[4]arene and 4.08 g (30 mmol) of sodium acetate trihydrate in 26 mL of MeOH–DMF (5:8 v/v), the diazo salt solution was added to give a red suspension, the red reactant was allowed to couple for 2 h more in an ice bath, then acidified by 150 mL of aqueous HCl and warmed at 60 °C for 30 min to produce reagent **1** in a quantitative yield as a reddish viscous solid. The solvent was evaporated to dryness, the treatment of the residue with chloroform gave a precipitate. After filtered out it was dissolved by methanol, the insoluble solid was removed and a new precipitate performed when chloroform was added, then the pure product was obtained by filtration. mp > 300 °C. IR, ν: 3432 (OH), 1594 (N=N), 1187 and 1038 cm^{-1} (SO_3^-). ^{1}H NMR (D_2O), δ (ppm): 4.2 and 4.9 (CH_2, AB q, 8 H), 7.9–8.5 (Ar, m, 24 H), 9.2 (s, 4 H, ArOH). Elem. Anal. Calcd for $C_{52}H_{36}O_{16}N_8S_4Na_4 \cdot H_2O$ (%): C, 49.29; H, 3.00; N, 8.85; Found (%): C, 49.02; H, 2.89; N, 8.96.