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Calix[4]arene based fluorescent chemosensor bearing coumarin as fluorogenic unit: Synthesis, characterization, ion-binding property and molecular modeling

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ABSTRACT

A series of calix[4]arene-based fluorescent chemosensors in cone and 1,3-alternate conformations have been synthesised incorporating ethylene glycol units as binding sites and coumarin as fluorescent probe. These compounds have been designed with variation in substituents, conformations of the calixarene unit and steric crowding. The open chain ethylene glycol moieties are flexible so that they can orient themselves in space to make effective interactions with metal ions. Ion-binding study of these fluoroionophores has been carried out using a large number of metal ions and the ion recognition event is monitored by fluorescence and absorption spectroscopy. Substantial quenching in emission intensity in presence of Fe^{3+} and Cu^{2+} and enhancement of emission intensity in presence of Ca^{2+} suggests strong binding of these metal ions with the ionophores. Complexation with these metal ions is also evident from UV–Vis spectral changes. Composition of the complexes formed (1:1) has been confirmed by ESMS analysis. Binding constants with the strongly interacting metal ions have been evaluated from fluorescence titration data. DFT calculations have been carried out to find out the metal binding sites of the calix ionophores and frontier molecular orbital analyses have rationalized the fluorescence behaviors observed upon complexation with metal ions in these cases.

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1. Introduction

The development of molecular sensors for efficient detection of specific metal ion is an emerging area in chemistry because of their role in various chemical, environmental and biological processes [1–5]. Various analytical techniques that are available for the detection of metal ions in low concentration includes atomic absorption spectrometry, spectrophotometry, inductive coupled plasma spectrometry, ion chromatography, voltammetry, etc.; however many of these methods are not simple and suitable for quick and online analysis. In recent years, fluorescent molecular sensors have attracted much attention because of the advantages of ease of detection, high sensitivity and instantaneous response [1–8]. This method of detection requires photo responsive ionophore, which can be developed by covalent linking of a luminescent molecule with the ionophore and the photophysical property of the fluoroionophore perturbs during the recognition process producing changes in luminescent emission. Among various ionophores, calixarenes are found to be very attractive because modifications of calixarenes give rise to a great variety of derivatives with various functional groups and these modified calixarenes provide a highly preorganized architecture for the assembling of converging binding sites [5,9–15]. For example, calix[4]arene derivatives with crown ethers, azacrown ethers, esters and amides have shown to form complexes with metal ions with high selectivity [16–28].

Among various transition metal ions, Fe^{3+} is one of the most important one as it plays crucial role in a variety of cell functions including oxygen carrying capacity of heme and electron transfer processes in DNA and RNA syntheses [29,30]. Deficiency and excess of iron in human body can induce a variety of diseases; therefore its detection is very important [30]. The examples of Fe^{3+} selective fluorescent sensors are not many compared to other metal ions and majority of them have been reported recently [31–45]; among them the examples of calixarene as ionophore are scarce [36–45]. Cu^{2+} is another metal ion, which plays important role in various biological and environmental processes [46]. It is also toxic to human body at higher concentration and can causes a number of liver and kidney related diseases [47,48]. Therefore, detection of this metal ion is also important, however examples of fluorescent sensors for Cu^{2+} are relatively high compared to Fe^{3+} [9,10,36,37,44,49,50].

With the aim to develop fluorescent molecular sensors for these metal ions, the calix[4]arene has been modified incorporating

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ethylene glycol moieties as binding sites, as this metal ion prefers to bind with oxygen atoms, and coumarin unit is attached with the glycol moiety as fluorescent probe. These compounds have been designed with variation in number of substituents, length of ethylene glycol moieties and conformations of the calixarene unit; and also *tert*-butylcalix[4]arene is used in one case to impose controlled amount of steric crowding, a secondary crown ether unit is also incorporated in another compound to introduce a secondary ionophore. The substituents are non-macrocyclic and flexible so that they can orient themselves in space to make effective interactions with metal ions. The performance of this series of fluoroionophores has been investigated with a large number of metal ions and all of them exhibited strong interactions with Fe^{3+}, a few of them with Cu^{2+} and Ca^{2+}. Herein we report synthesis, characterization and ion-binding property of a series of fluoroionophores and also DFT calculations and frontier molecular orbital analyses to rationalize observed fluorescence behavior of the compounds.

2. Experimental

2.1. Materials

All the starting materials were purchased either from Sigma Aldrich Company or from S.D. Fine Chemicals. All the perchlorate salts of the cations were purchased from Alfa Aesar (Johnson Matthey Company). Analytical thin-layer chromatography was carried out on silica gel plates (SiO_2, Merck 60 F_{254}) obtained from E. Mark Chemical Co. All organic solvents were analytical grade and used as received for synthesis work; and purified by standard procedures for spectroscopic study. The starting compounds *tert*-butylcalix[4]arene and calix[4]arene were synthesized following the published procedures [51,52].

2.2. Physical measurements

Elemental analyses (C, H, and N) were performed on a model 2400 Perkin–Elmer or model Vario Micro Cube from Elementar elemental analyzer. Mass spectra were recorded on a Q-TOF Micro™ LC–MS instrument. Infrared spectra were recorded on a Perkin–Elmer spectrum GX FT-IR spectrophotometer as KBr pellets. NMR spectra were recorded on models DPX 200 and Avance II 500 Brucker FT-NMR instruments. The UV–Vis spectra were recorded on a model CARY 500 SCAN (Varian) and UV-3101PC (Shimadzu) UV–Vis–NIR spectrophotometers. Luminescence spectra were recorded on a model Fluorolog Horiba Jobin Yvon spectrofluorimeter at room temperature.

Caution: Perchlorate salts of metal ions are potentially explosive. Therefore, they should be handled with great care.

2.3. Synthesis of intermediate compounds (***A–I***)

The intermediate compound **A** was synthesised following the method described below. The other intermediate compounds **B**–**I** were synthesised following the published procedures reported by us and others [21,53–55].

2.3.1. Synthesis of compound ***A***

In a solution of calix[4]arene (1 g, 2.36 mmol) in CH_3CN (90 mL), 2-(2-chloroethoxy)ethyl4-methylbenzenesulfonate (0.836 g, 3 mmol) and K_2CO_3 (0.415 g, 3 mmol) were added and the reaction mixture was heated at reflux for 24 h under inert atmosphere. The solution was then allowed to cool to room temperature and evaporated to dryness by rotary evaporation. The residue was dissolved in $CHCl_3$ (150 mL) and treated with 5% aqueous HCl (100 mL), the non-aqueous layer was then separated and washed twice with water. The organic layer was dried over anhydrous sodium sulfate and evaporated. The compound was purified by column chromatography on silica gel (100–200 mesh) using 1:9 (v/v) ethyl acetate/hexane as eluent. Yield: 0.876 g, (70%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H, Ar–*OH*), 9.23 (s, 2H, Ar–*OH*), 7.09 (d, 2H, $J = 7.5$ Hz, Ar–H_m), 7.04 (d, 2H, $J = 7.5$ Hz, Ar–H_m), 7.0 (d, 4H, $J = 7.5$ Hz, Ar–H_m), 6.80 (t, 1H, $J = 7.5$ Hz, Ar–H_p), 6.70–6.65 (m, 3H, Ar–H_p), 4.46 (d, 2H, $J = 13.0$ Hz, Ar–CH_2–Ar), 4.33 (br-s, 2H, Ar–O–CH_2–CH_2–), 4.27 (d, 2H, $J = 13.0$ Hz, Ar–CH_2–Ar), 4.14 (br-s, 2H, Ar–O–CH_2–CH_2), 3.99 (t, 2H, $J = 5.0$ Hz, –O–CH_2–CH_2–Cl), 3.79 (t, 2H, $J = 5.0$ Hz, –O–CH_2–CH_2–Cl), 3.46 (d, 2H, $J = 13.0$ Hz, Ar–CH_2–Ar), 3.45 (d, 2H, $J = 13.0$ Hz, Ar–CH_2–Ar. ESMS (*m/z*): found 569.21(40%) Calc. for $[\mathbf{A} + K^+]$ 570.14, found 553.23 (50%) Calc. for $[\mathbf{A} + Na^+]$ 554.03, found 531.24 (100%) Calc. for $[\mathbf{A} + H^+]$ 532.04. *Anal.* Calc. for $C_{32}H_{31}ClO_5$: C, 72.4; H, 5.9. Found: C, 73.1; H, 5.7%.

2.4. Synthesis of compounds ***1–6***

2.4.1. Synthesis of compound ***1***

In a solution of the intermediate compound **A** (0.265 g, 0.5 mmol) in acetone (70 mL), 7-hydroxy-4-methyl coumarin (0.140 g, 0.8 mmol), K_2CO_3 (0.276 g, 2 mmol) and catalytic amount of potassium iodide (5 mg) were added and the reaction mixture was heated at reflux for 2 days under nitrogen. The solution was then allowed to cool to room temperature and evaporated to dryness by rotary evaporation. The residue was extracted 3 times with water–$CHCl_3$ mixture. The organic layer was dried over anhydrous sodium sulfate and evaporated. The compound was purified by column chromatography on silica gel (100–200 mesh) using 1:1(v/v) ethyl acetate/hexane as eluent. Yield: 0.178 g, (53%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.84 (s, 1H, Ar–*OH*), 9.21 (s, 2H, Ar–*OH*), 7.36 (d, 1H, $J = 9.5$ Hz, coumarin–*H*), 7.07 (d, 2H, $J = 7.5$ Hz, Ar–H_m), 7.01–6.96 (m, 6H, Ar–H_m), 6.86 (t, 1H, $J = 7.5$ Hz, Ar–H_p), 6.82 (s, 1H, coumarin–*H*), 6.82–6.80 (overlapped signal, 1H, coumarin–*H*), 6.67 (t, 1H, $J = 7.0$ Hz, Ar–H_p), 6.63 (t, 2H, $J = 7.0$ Hz, Ar–H_p), 6.11 (s, 1H, coumarin–*H*), 4.45 (d, 2H, $J = 13.0$ Hz, ArCH_2Ar), 4.39–4.35 (m, 4H, –CH_2CH_2O–coumarin (2H) and Ar–O–CH_2–CH_2– (2H)), 4.20–4.18 (m, 4H, ArCH_2Ar (2H) and Ar–O–CH_2–CH_2– (2H)), 4.12 (t, 2H, $J = 4.0$ Hz, –O–CH_2–CH_2–O–coumarin,), 3.41 (d, 4H, $J = 13.0$ Hz, ArCH_2Ar), 2.35 (s, 3H, coumarin–CH_3), ESMS (*m/z*): found 671.96 (40%) Calc. for $[\mathbf{1} + H^+]$ 671.75. *Anal.* Calc. for $C_{42}H_{38}O_8$: C, 75.2; H, 5.7. Found: C, 75.4; H, 5.6%.

2.4.2. Synthesis of compound ***2***

The compound **2** was synthesized from the intermediate **B** following the similar method as described for **1**, except the ratio of reactants, refluxing time and purification procedure. In this case, 0.352 g (2 mmol) of 7-hydroxy-4-methyl coumarin and K_2CO_3 (0.553 g, 4 mmol) were added, the reaction mixture was refluxed for 3 days and the crude product was purified by column chromatography on silica gel (100–200 mesh) using 3:2 (v/v) ethyl acetate/hexane as eluent. Yield: 0.23 g (50%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 2H, Ar–*OH*), 7.33 (d, 2H, $J = 8.5$ Hz, coumarin–*H*), 7.12 (d, 4H, $J = 7.5$ Hz, Ar–H_m), 7.07 (d, 4H, $J = 7.5$ Hz, Ar–H_m), 6.99 (s, 2H, coumarin–*H*), 6.86 (d, 2H, $J = 7.5$ Hz, coumarin–*H*), 6.73–6.61 (m, 4H, Ar–H_p), 6.11 (s, 2H, coumarin–*H*), 4.40 (d, 4H, $J = 13.0$ Hz, ArCH_2Ar), 4.26 (t, 4H, $J = 4.5$ Hz, Ar–O–CH_2–CH_2), 4.1 (t, 4H, $J = 4.5$ Hz, –CH_2–CH_2–O–coumarin), 3.63–3.59 (m, 8H, CH_2–CH_2–O–CH_2–CH_2–), 3.44 (d, 4H, J = 13.0 Hz, ArCH_2Ar), 2.35 (s, 6H, coumarin–CH_3) ESMS (*m/z*): found 956.74, Calc. for $[\mathbf{2} + K^+]$ 956.10, found 939.74 (100%), Calc. for $[\mathbf{2} + Na^+]$ 939.99. *Anal.* Calc. for $C_{56}H_{52}O_{12}$: C, 73.4; H, 5.7. Found: C, 72.9; H, 5.5%.

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