Publications / Symposia / Conferences
A. **Paper Published /Communicated:**


11. Selective Colorimetric Detection of Iodide (I⁻) and Cr³⁺ Ions from Aqueous Media With Calixarene Functionalized Gold Nanoparticles. Debdeep Maity, A. Kumar, R. Gunupuru, P. Paul. (manuscript under submission).


B. Papers presented in Conferences/Symposium:


Effect of steric crowding on ion selectivity for calix-crown hybrid ionophores: experimental, molecular modeling and crystallographic studies†

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A number of calix[4]arene-azacrowns with variation in ring size and substituents at the upper and lower rims have been synthesized to investigate the effect of steric crowding towards ion selectivity. The structural elucidation of these ionophores has been carried out mainly by $^1$H NMR and ES-MS in solution and by single crystal X-ray study in the solid state. Interaction of these ionophores with a large number of cations has been investigated by NMR studies. The ionophore with tert-butyl at the upper rim (3) exhibits selectivity towards Na$^+$ only whereas an ionophore of the same size but without tert-butyl at the upper rim (1) shows selectivity towards both Na$^+$ and K$^+$. An ionophore of the same size but with three tosyl substituents at the lower rim (4) exhibits no complexation with any cation. The ionophore with the larger crown ring and without tert-butyl at the upper rim (2) exhibits complexation with K$^+$, Rb$^+$, Ba$^{2+}$ and weak interaction with Na$^+$. Binding constants with these metal ions have been determined by NMR titration. Molecular modeling studies performed by a molecular mechanics force field (MMFF94) using the Monte Carlo search method and DFT calculations predicted the observed higher selectivity for sterically crowded receptor.

Introduction

Calixarenes, cyclic oligomers made up of phenol units linked by a methylene bridge, are receiving increasing attention because of their potential use as hosts for sensing various analytes.1-5 In the calixarene family, calix[4]arenes are the most popular because of their rigid structures, which make them ideal candidates for complexation with various ions.6-9 This chemistry has become more versatile because of the ease with which calix[4]arene can be modified with functional groups at lower and upper rims, depending on the requirement. These modified calixarenes provide a highly preorganized architecture for the assembling of converging binding sites.10-14 Among calixarene derivatives, calix[4]arene-crown hybrid molecules have attracted intense interest because of their remarkable selectivity towards alkali and alkaline earth metal ions.15-22 The ion selectivity of this class of compounds is controlled mainly by the conformation of the calixarene platform, the size of the crown ring and the substituents at the upper and lower rims of the calixarene unit. Incorporation of the substituents at the –OH groups of the lower rim suppresses hydrogen-bonding and increases steric hindrance, which results in the formation of conformational isomers such as cone, partial-cone, 1,3-alternate and 1,2-alternate.15,23-28 In the cone conformation, the appended functional groups at the two sides of the crown ring and in the 1,3-alternate conformation the substituents attached to the crown moiety play an important role to determine selectivity.8,16,19,21,22 Among various size of crown rings, crown-5 and crown-6 containing calixarene derivatives are found to be more suitable for complexation with alkali-metal ions.15,18,21,22

Another class of calix-crown based receptors, in which a nitrogen atom is incorporated in the crown ring has been developed. The presence of a nitrogen atom in the crown ring provides an advantage for attaching desired substituents for a specific study - inclusion of photoactive substituents produced a new class of luminescent molecular sensor and it has been widely used to monitor ion recognition events.16,22,29-32 Apart from luminescence output, the substituents also play an important role in the determination of selectivity, e.g. N-chromogenic calix[4]arene azacrown, in which a 2-hydroxy-5-nitrobenzyl group attached on nitrogen, exhibited high potassium selectivity over other metal ions and it was assumed that the OH of the chromogenic group assisted the complexation by encapsulating the metal ion.16 Another series of calix[4]arene azacrown ethers has been reported in which 2-picolyl, 3-picolyl and benzyl groups were attached on the nitrogen atom and among these compounds, the 2-picolyl armed calixazacrown ether showed the highest selectivity towards silver ions due to electrostatic interactions by encapsulation of the metal ion assisted by the nitrogen atom of the 2-picolyl group.29 When pyrene was attached to

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† Electronic supplementary information (ESI) available: H-bonding table (Table S1), packing diagrams of 3 and 4 (Fig. S1 and S2), lowest energy conformer of 4 with Na$^+$ and K$^+$ (Fig. S3), CCDC reference numbers 749549–749552. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00587k
Calix[4]arene based molecular sensors with pyrene as fluoregenic unit: Effect of solvent in ion selectivity and colorimetric detection of fluoride

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Dedicated to Prof. S.S. Krishnamurthy.

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Fluorescent molecular sensors having excimer emission property have been designed and synthesised incorporating calix[4]arene derivatives in cone and 1,3-alternate conformation as ionophore and two pyrene moieties at close proximity as fluorophore. They exhibit strong excimer emission around 515 nm, which is used to monitor interaction of metal ions with the ionophores. Ion-binding study of these fluoroionophores has been investigated in acetonitrile–chloroform and THF–H2O with a wide range of cations and anions and the recognition process is monitored by luminescence, UV–Vis and 1H NMR (for F\textsuperscript{−}) spectral changes. The present study demonstrated profound influence of solvent in ion selectivity, in acetonitrile–chloroform they formed complexes with Hg\textsuperscript{2+}, Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Ni\textsuperscript{2+}, whereas in THF–H\textsubscript{2}O they exhibit selectivity only for Cu\textsuperscript{2+}. In the case of anions, selectivity for only F\textsuperscript{−} with color change is observed. Composition of the complexes formed was determined from mass spectrometry and the binding constants were determined from fluorescence titration data. The reasons for formation of excimer emission, quenching of it in presence of certain metal ions, role of solvent in selectivity and energy/electron transfer process involved in the ion-recognition event have been discussed on the basis of experimental data.

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1. Introduction

Development of molecular sensors for detection of specific metal ion is an emerging area in research because of their potential applications in various fields of chemistry, biology and environmental processes [1–5]. Among various available methods, detection by fluorescent technique has been widely used because of some distinct advantages in terms of sensitivity, selectivity, response time, in-situ monitoring, etc. [1,5]. Fluorescent molecular sensors can be constructed by the combination of an ionophore, designed for the binding of specific incoming ion, and a fluorogenic unit whose photophysical properties perturbs during the recognition process to produce a measurable output signal. In designing of fluorescent sensors, an interesting approach is to attach two aromatic fluorophores in proximity so that they are close enough (within van der Waals contact) to make interaction such as π–π stacking. Under this condition, electronic excitation of one ring can cause an enhanced interaction with its neighbor, leading to what is termed as excited-state dimer or excimer [5,6]. This excimer typically provides a broad fluorescence band with the maxima at lower energy compared to emission from monomer and this band can be used to read out the molecular recognition process more conveniently [7,8]. In general, highly π-delocalized planar systems such as pyrene and naphthyl moieties have been used for this purpose, they exhibited intramolecular excimer due to strong π–π interaction between two fluorophore units and this excimer emission perturbed in presence of guest ions [9,11–15]. It has been reported that the excimer emission is strongly quenched upon addition of Pb\textsuperscript{2+} and Fe\textsuperscript{3+} [9,11–15] whereas significant enhancement of excimer emission intensity is reported for metal ions such as Ln\textsuperscript{3+}, K\textsuperscript{+} and Li\textsuperscript{+} and anion like F\textsuperscript{−} [10–12,14].

Ionophore is an important component in designing molecular sensors, its donor atoms, conformation, size, steric hindrance etc. determines selectivity. Among various ionophores, macrocyclic ligands are noted for their remarkable selectivity towards cations making them excellent choices for selective binding of metal ions [1,3,16]. In this regard, calixarenes are found to be very attractive because modifications of calixarene gives rise to a large variety of derivatives with various functional groups, which provide a highly preorganized architecture for the assembling of converging binding sites [5,17–19,20].

With a view to develop calixarene based fluoroionophores with excimer emission, two compounds have been synthesised incorporating pyrene moieties at close proximity and with variation in conformation in the calixarene unit. Here we report synthesis and characterization of these molecules and their ion-binding property with a large number of cations and anions, effect of solvents and conformation of the ionophores on ion-selectivity, and
Synthesis and anion-sensing property of a family of Ru(II)-based receptors containing functionalized polypyridine as binding site

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A family of fluoroionophores have been synthesized incorporating Ru(II)-bipyrindine moiety as fluorogenic unit and amino/benzenesulphonamido functionalized 1,10-phenanthroline moiety, attached to Ru(II), as binding sites. Two of the ligands and one of the complexes have been characterized crystallographically. Anion recognition property, studied by luminescence, UV-vis and 1H NMR spectroscopy, with a large number of anions exhibit strong complexation with F−, H2PO4− and AcO−. Binding constants have been determined from luminescence titration and 1H NMR study gave insight about binding site of anions. Bidentate chelating nature of the H2PO4− and AcO− anions and steric crowding created by benzenesulphonamide moiety has significantly influenced binding constants and selectivity.

The design and synthesis of artificial receptors for recognition and sensing of anions has received considerable interest in recent years because of the important role played by anions in biological, environmental and industrial processes [1]. In designing of anion receptors, various noncovalent interactions, such as hydrogen-bonding, electrostatic, hydrophobicity, are mainly considered to make interaction between binding sites and anions [2]. To monitor recognition event, fluorescent technique is gaining increasing attention because of high sensitivity and easy online monitoring. Binding of ions to the recognition sites leads to changes in photophysical properties of the receptors that serve as indicator for ion-recognition [2,3]. As fluorogenic unit, photoactive organic molecules have been widely used [1,4], however fluorescent metal complexes such as ruthenium(II)-polypyridine moiety can also be used [1–3,5]. For anion recognition, the latter has some advantages over organic molecules, the positive charge on the metal ion makes electrostatic interaction with negatively charged species leading to strong host–guest interaction.

We have designed fluoroionophores incorporating Ru(II)-polypyridine moiety as fluorogenic unit and functionalized 1,10-phenanthroline moiety containing amino (—NH2) and benzenesulphonamide groups as binding sites for anion recognition. We report here synthesis, characterization, electrochemical and ion-recognition properties of these fluoroionophores.

The compound 5,6-diamino-1,10-phenanthroline (L1) was prepared following the literature procedure [6] and the benzenesulphonamide derivatives (L2–L4) were prepared following the modified published procedure (Scheme 1) used for other systems [7]. It may be noted that the excess benzenesulfonylchloride used in the reaction was hydrolyzed under the reaction conditions to benzenesulfonic acid, the acidic hydrogen atom of which combined with —NH2 of the ligand to form —NH3+ and isolated as organic salt with deprotonated benzenesulfonic acid as counter anion, [L2H+][C7H7SO3−], [L3H+][C7H7SO3−] and [L4H+][C6H5SO3−]. The elemental analysis (C, H, and N) and mass spectrometric data are in excellent agreement with the compositions of the ligands. As expected, the mass spectrometric data are corresponding to the cationic part of the ligand. In the 1H NMR spectra, the signals for —NH3+ and NH protons appeared around δ 6.5 and 10.0, respectively and the deprotonated benzenesulfonic acid exhibits two doublets in the regions δ 7.4–7.7. The metal complexes [Ru(bpy)2Cl2]2+ and [Ru(bpy)2Cl2]2H2O (L=L1 (1), L2 (2), L3 (3) and L4 (4)) were synthesized by the reaction of cis-[Ru(bpy)2Cl2]2H2O with the respective ligand (L1 and salts of L2/L3/L4) in ethanol-water under reflux, isolated as PF6− salt and purified by column chromatography [8]. The complexes, however did not show the presence of —NH3+, the deprotonation took place under the reaction conditions with the building block cis-[Ru(bpy)2Cl2]. The elemental analysis (C, H and N) are in agreement with the compositions of the complexes and the mass spectrometric data correspond to the mass of [M-PF6]+ and the 1H NMR spectral data are consistent to the structures shown in Fig. 1.

Crystals for [L2H+][C7H7SO3−] and [L3H+][C7H7SO3−] were grown from CH3CN/MeOH and the data analysis [9] confirmed the structures shown in Fig. 2. The ORTEP views of these compounds clearly show that the amino nitrogen of the ligand is protonated forming cation and deprotonated benzenesulfonic acid acts as counter anion. Crystals
Calixarenes: Versatile molecules as molecular sensors for ion recognition study

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Abstract. This article presents a brief account on designing of calixarene-based molecular sensor for recognition of various metal ions and anions and also different analytical techniques to monitor the recognition event. This review focuses only on calix[4]arene derivatives, in which mainly the lower rim is modified incorporating either crown moiety to make calix–crown hybrid ionophore to encapsulate metal ions or some fluorescent inorganic and organic moieties to use it as signalling unit. In order to investigate effect of conformation of the calixarene unit and steric crowding on ion selectivity, designing of these molecules have been made using both the cone and 1,3-alternate conformations of the calixarene unit and also incorporating bulky tert-butyl group in few cases to impose controlled steric crowding. Among various ions, here focuses are mainly on biologically and commercially important alkali metal ion such as K\(^+\), toxic metal ions such as Hg\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), important transition metal ion such as Cu\(^{2+}\) and toxic anion like F\(^-\). The techniques used to monitor the recognition event and also to determine binding constants with strongly interacting ions are fluorescence, UV-vis and \(^1\)H NMR spectroscopy. Most of the ionophores reported in this review have been characterized crystallographically, however no structural information (except one case) are incorporated in this article, as it will occupy space without significant enhancement of chemistry part. Different factors such as size of the ionophore cavity, size of metal ion, coordination sites/donor atoms, steric crowding and solvents, which determine selectivity have been discussed. Response of ion recognition process to different analytical techniques is another interesting factor discussed in this article.

Keywords. Molecular sensor; calixarene; ion recognition; fluoroionophores; supramolecular chemistry.

1. Introduction

Design and synthesis of functional molecules that could serve as molecular devices for sensing of specific ion is an area of intense activity in current research.\(^1\) Different types of organic molecules have been used as ionophore to design molecular sensor, however, macrocyclic ligands are excellent choices for this purpose because of their remarkable selectivity towards various metal ions. In this regard, calixarenes, which are macrocyclic oligomers made up of phenol units linked by methylene bridge are found to be very attractive because of their ability to bind variety of ions.\(^1,2\) In the calixarene family, calix[4]arenes are most popular because of their rigid structures, which make them ideal candidates for the complexation with metal ions (1).\(^2,3\) Both the upper and lower rims of the calixarene can be modified depending on the requirement and these modified calixarenes provide a highly preorganized architecture for the assembling of converging binding sites.

Ion-selectivity of the calixarenes are controlled by different factors such as conformation of the calix moiety (2), binding sites, size of the ionophore cavity, steric crowding, solvent used and also response of the recognition event to different analytical techniques. We have been working in this area for last few years and have synthesized series of new molecular sensors incorporating calix[4]arene derivatives as ionophore.\(^5,6,8,11\) The ion-recognition property of all these molecules has been investigated with a wide range of cations and anions and the recognition event was monitored by various spectroscopic techniques. On the basis of our study, we report here a brief account of the various aspects of design and ion-selectivity of calixarene derivatives as molecular sensor.

2. Design of receptors for selective recognition of alkali and alkaline earth metal ions

For the recognition of alkali and alkaline earth metal ions, a new class of hybrid molecule has been developed incorporating crown ethers into calix[4]arene.\(^5,6,8,11\) The
Calix Receptor Edifice; Scrupulous Turn Off Fluorescent Sensor for Fe(III), Co(II) and Cu(II)

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Abstract Novel Supramolecular fluorescence receptor derived from calix-system i.e. calix[4]resorcinarene bearing dansylchloride as fluorophore was designed and synthesized. The compound was purified by column chromatography and characterized by elemental analysis, NMR and Mass spectroscopy. Tetradansylated calix[4]resorcinarene (TDCR) shows a boat conformation with C2v symmetry. The complexation behaviour of metal cations [Ag(I), Cd(II), Co(II), Fe(III), Hg(II), Cu(II), Pb(II), Zn(II), U(VI) (1×10^-4 M)] with tetra dansylated calix[4]resorcinarene (1×10^-6 M) was studied by spectrophotometry and spectrofluorometry. Red shift in the absorption spectra led us to conclude that there is strong complexation Fe(III), Co(II) and Cu(II) with TDCR. These metal cations also produce quenching with red shifts in the emission spectra. The maximum quenching in emission intensity was observed in the case of Fe(III) and its binding constant was also found to be significantly higher than that of Co(II) and Cu(II). Quantum yield of metal complexes of Fe(III) was found to be lower in comparison with Co(II) and Cu(II) complexes. Stern Volmer analysis indicates that the mechanism of fluorescence quenching is either purely dynamic, or purely static.

Keywords Fluorescent Quenching · Calix[4]resorcinarene · Ion-binding · Dansyl chloride

Introduction

The development of selective artificial fluorescence receptors for the detection of biologically and environmentally important metal ions has been an important goal in the field of supramolecular chemistry [1] and chemical sensors [2]. Fluorescent chemosensors typically consist of an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore) linked through the proper spacer [3], are also called as fluoroionophore [4]. The ionophore is required for selective binding of the substrate, while the fluorophore provides the means of signaling this binding, either by fluorescence enhancement or quenching [5, 6]. The ideal fluorophore in chemosensors has high quantum yields of fluorescence, high extinction coefficients, long excitation and emission wavelengths, a long lifetime and photostability. Therefore, the choice of fluorophore is the most important factor in the design of new fluorescent chemosensors [7]. Different chemosensors have been used for investigation of their selective fluorescent responses upon complexation with various cations [8, 9]. Recently, there has been strong interest in dansyl derivatives as potential fluorophores [10–13]. Dansyl chloride is an attractive fluorophore due to the strong fluorescence, relatively long emission wavelength (Em=400–600 nm), Stokes shift (Ex=330–350 nm) and is also easy to introduce in a molecular skeleton to obtain fluorescent sensors [14]. Calixarenes [15, 16] which are cyclic oligomers of phenolic and methylene moieties, their preorganized binding...

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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 [5–15]. 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(III) 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(III) 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(II) 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(II) are relatively high compared to Fe(III) [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...