



Calix[4]arene-based ditopic receptors for simultaneous recognition of fluoride and cobalt(II) ions

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ABSTRACT

A series of calix[4]arene based ditopic receptors possessing bipyridyl and hydrazone units have been synthesized and evaluated for ionic recognition. It has been observed that the synthesized derivatives function as allosteric receptors for simultaneous recognition of Co^{2+} and F^- ions through non-covalent interactions. Significant bathochromic shifts in the UV–visible spectrum with a profound colour change promise their use to engineer novel applications.

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Introduction

The design and synthesis of ditopic molecular receptors for simultaneous sensing of cationic and anionic species constitute important challenges in supramolecular chemistry. Such receptors find inherent applications in salt solubilization, ionic extraction, transport phenomenon and the development of molecular devices.¹ A ditopic molecular host exhibits cooperative binding of cationic and anionic species through allosteric effects wherein binding of one ion markedly influences the binding of the other ion.² Amongst such receptors for cations, the ones having capability for the recognition of transition metal ions have special fascination since they are toxic when present in excess but are essential in small amounts (such as iron, cobalt, copper and zinc) for the living systems.^{1a,3} Similarly, amongst anions, the fluoride ion evinces major interest due to its ubiquitous detrimental and beneficial role in human health and the environment.⁴

Amongst several approaches adopted for the development of ditopic receptors, the most important one consists of combining the crown ethers (to bind cations) and functions containing urea, thiourea and amide linkages (for the recognition of anions through N–H–X hydrogen bonds).⁵ Since the electronic charge on anions is more polarized than cations, one would expect that the cation and anion binding would be sequential in nature.

Bipyridyl compounds are known to form strong complexes with transition metal ions under specific pH conditions⁶ and hydrazones

are known to form complexes with anions.⁷ A combination of bipyridyl and hydrazone units in a suitable macrocycle scaffold would therefore be expected to yield ditopic receptors for the recognition of both cations and anions simultaneously. In this context we stipulated that the calix[n]arene scaffold⁸ would offer a suitable molecular architecture for the development of ditopic receptors^{1a,9} since they can be functionalized to incorporate appropriate and complementary binding sites with well defined conformational characteristics to facilitate interaction with targeted guest species.

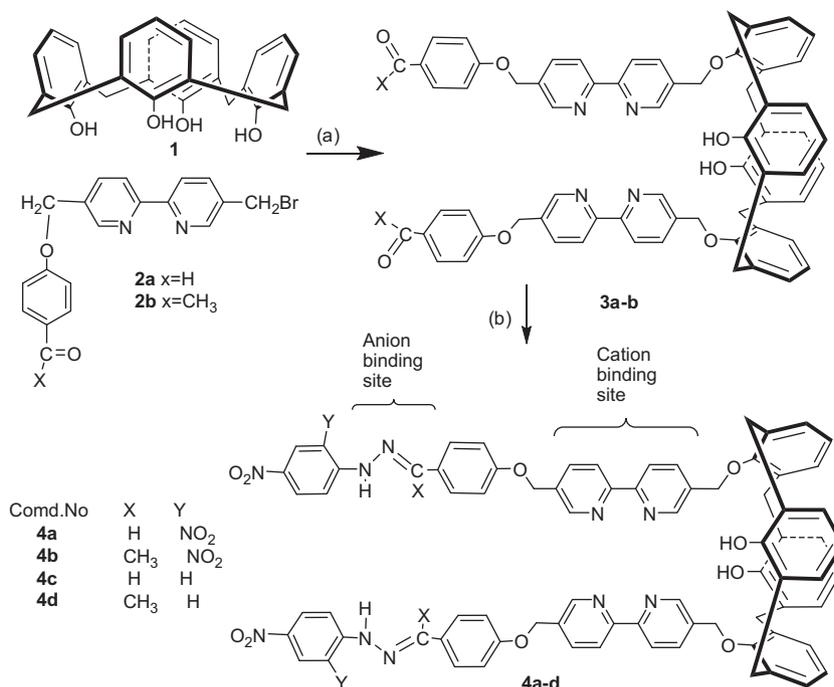
In this Letter, we report the synthesis and evaluation of a series of novel calix[4]arene based ditopic receptors (**4a–d**) for the simultaneous binding of F^- and Co^{2+} ions with a significant bathochromic shift and distinct ‘naked eye’ colour change. To the best of our knowledge, this is the first report on the utilisation of bipyridyl and hydrazone bearing calixarene scaffolds for target applications.

Calix[4]arene **1** was obtained by utilizing the synthetic protocols available in the literature¹⁰ while **2a** and **2b** were synthesized by following the synthetic route depicted in Scheme S1 (Supplementary data). Compounds **2a** and **2b** were separately refluxed with calix[4]arene (**1**) in the presence of K_2CO_3 in CH_3CN for 48–96 h to give **3a–b** in good yields (86%). Reaction of **3a** and **3b** with phenylhydrazines¹¹ gave **4a–d** in 88–92% yields (Scheme 1).

The receptors **4a–d** gave characteristic spectroscopic analysis for their indicated structures. For instance **4a** gave a $>\text{C}=\text{N}-$ signal at 1605 cm^{-1} and a sharp pair of doublets at δ 3.52 and δ 4.24 for axial and equatorial protons respectively in the ^1H NMR spectrum and a distinct signal at δ 30.6 for the methylene carbons in its ^{13}C NMR spectrum to indicate a symmetric cone conformation for the calix[4]arene scaffold.^{11,12} The structure of **4a** was indicated by the

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Scheme 1. Synthesis of compound **4a–d**. Reagents and conditions: (a) K₂CO₃, CH₃CN, reflux, 16 h; (b) phenylhydrazine derivatives, ethanol.

appearance of two singlets for the CH₂-bpy and OCH₂-bpy at δ 5.13 and δ 5.29, two triplets at δ 6.62 and δ 6.85 and two doublets at δ 7.01 and δ 7.19 for aromatic protons of calix[4]arene skeleton. It was further confirmed by observing D₂O exchangeable singlets at δ 8.52 and δ 11.3 which could be attributed to of –NH and –OH protons, respectively. A non deuteratable singlet at δ 7.59 for azo-methine proton (–N=CH) confirmed the structure for **4a** as depicted in Scheme 1.

The cation and anion binding characteristics of receptors **4a–d** were examined by UV–visible spectroscopy in DMSO:CH₃CN (0.5:9.5 v/v). It showed two absorption peaks at 287 and 388 nm that could be attributed to the absorption maxima for the bipyridyl⁸ and hydrazone¹⁰ units present.

The anion binding ability of **4a–d** was examined for various anions by using tetrabutylammonium salts of F[–], Cl[–], Br[–], I[–], HSO₄[–], ClO₄[–] and PF₆[–] in DMSO:CH₃CN (0.5:9.5 v/v). It was determined that the receptor **4a** very selectively recognises the fluoride ion from a mixture of various commonly encountered anions

(Fig. 1a). For example, when 2×10^{-5} M solution of **4a** was treated with tetrabutylammonium fluoride, it exhibited a significant bathochromic shift ($\Delta\lambda_{\text{max}}$) of 95 nm in its UV–visible spectrum with the appearance of a new peak at 483 nm while its absorption maxima at 388 nm remained unchanged with other anionic species (Cl[–], Br[–], I[–], HSO₄[–], ClO₄[–] and PF₆[–]) as shown in Figure 1a. It was observed that on gradual addition of a standard solution of tetrabutylammonium fluoride, the intensity of absorption peak at 388 nm progressively decreased while the intensity of the absorption peak at 483 nm increased simultaneously (Fig. 1b). However the interaction of **4a** with fluoride ions did not affect the absorption peak at 287 nm at all indicating that the F[–] ions possibly bind at the hydrazone NH binding sites through hydrogen bonds as observed earlier.^{10d}

The binding of **4a–d** with fluoride ions was found to be associated with visual colour changes which could be easily monitored through a ‘naked-eye’ as depicted in Figure 2. It was found that **4a** exhibited a prominent and instantaneous colour change

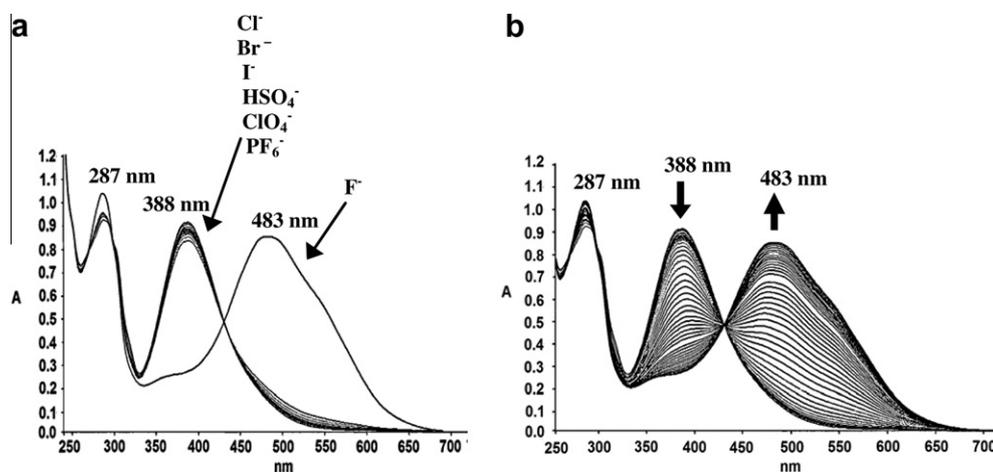


Figure 1. (a) Absorption spectra of **4a** (2×10^{-5} M) upon addition of F[–], Cl[–], Br[–], I[–], HSO₄[–], ClO₄[–] and PF₆[–] ions (as tetrabutylammonium salts) (1×10^{-4} M) in DMSO/CH₃CN (0.5:9.5 v/v) (b) UV–visible titrations of **6a** with 0–8 equiv of F[–].

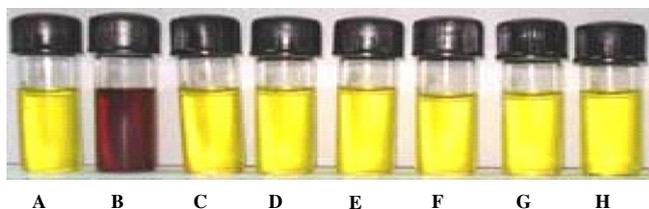


Figure 2. Selectivity of **4a** for fluoride ion over other anions. Colour changes of **6a** (20 μM) in DMSO/CH₃CN (0.5:9.5 v/v) with the addition of TBA anions (5×10^{-5}). A = free ligand, B = F⁻, C = Cl⁻, D = Br⁻, E = I⁻, F = HSO₄⁻, G = PF₆⁻, H = ClO₄⁻.

from light yellow to dark purple only with fluoride ion in DMSO/CH₃CN (0.5:9.5 v/v), while no such colour change was observed with other anions (such as Cl⁻, Br⁻, I⁻, HSO₄⁻, ClO₄⁻ and PF₆⁻) when used in the form of their tetrabutylammonium salts under similar experimental conditions. It was interesting to note that the addition of protic solvents (such as water or methanol) triggered the disappearance of the observed colour of **4a**-F⁻ complex with the immediate regeneration of the original colour of the receptor. This suggested that F⁻-calix[4]arene interaction did not involve any plausible covalent bond formation and that the complexation of the fluoride ion with **4a** was reversible in nature.

When solutions of **4a–d** in DMSO:CH₃CN (0.5:9.5 v/v) were individually treated with perchlorate and nitrate salts of transition and alkali metal ions (Co²⁺, Cu²⁺, Ag⁺, Fe³⁺, Ni²⁺, Na⁺, K⁺), only the cobalt ion (in the form of its perchlorate at 2×10^{-5} M concentration) exhibited a significant bathochromic shift of 21 nm at λ_{max} 287 nm with the appearance of a new absorption at 308 nm with no change in the absorption peak at 388 nm as depicted in Figure 3; this observation clearly indicated the involvement of bipyridyl binding sites with the minimum perturbation of the absorption peak at 388 nm.

Evaluation of interaction between metal ion and the synthesized molecular receptors through Job's plot revealed maximum complexation at 0.5 mol fraction of Co²⁺ ions indicating a 1:1 binding-stoichiometry. Similar behaviour was observed on the addition of standard solutions of Cu²⁺ and Ag⁺ ions. The association constants ($\log K$)¹³ of Co²⁺, Cu²⁺ and Ag⁺ ions upon complexation with receptors **4a–d** were calculated from the UV-visible titration experiments depicted in Table 1.

Since **4a** has been synthesized in such a way that it has two distinct binding sites that comprise of bipyridyl and the phenyl hydrazone units, it seems apparent that bipyridyl units interact with transition metal ions while phenyl hydrazone units strongly bind the F⁻ ions.

The molecular receptor **4a** seems to behave like enzyme mimic with allosteric sites for anions and cations. For example, when one binding site is blocked by an anion the other site becomes available

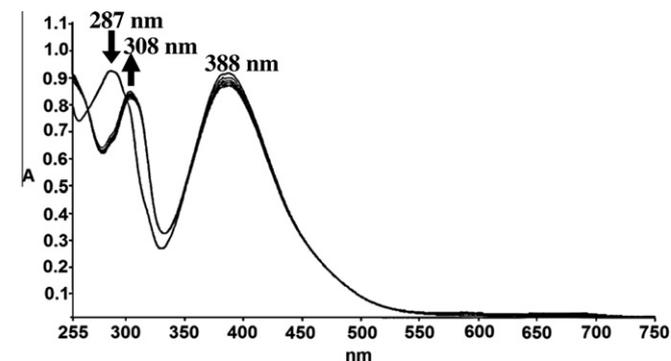


Figure 3. UV-visible titration curve of **4a** (2×10^{-5} M) upon addition of cobalt perchlorate (0–100 equiv) in DMSO/CH₃CN (0.5:9.5 v/v).

Table 1

Association constants from UV-vis titrations for complexes of receptors **4a–d** with cationic guests in DMSO:CH₃CN (0.5:9.5 v/v)^a

Receptor	Cations $\log K$ (M ⁻¹)		
	Co ²⁺	Cu ²⁺	Ag ⁺
4a	6.89	6.23	5.19
4b	6.73	6.02	4.89
4c	6.79	6.19	5.07
4d	6.68	6.00	4.79

^a The Co²⁺ and Cu²⁺ were added in the form of their perchlorate salts while Ag⁺ were added in form of its nitrate.

for cations. When the cation is bound with one of the sites, the other sites become available for binding anions. When both the sites have appropriate guest ions, the receptors become fully occupied. In the above context, therefore it was interesting to examine the behaviour of competing F⁻ ions and Co²⁺ ions on the binding ability of **4a**. Accordingly, the binding ability of receptor **4a** for F⁻ ions in the presence of Co²⁺ was examined by UV-visible spectroscopy in DMSO:CH₃CN (0.5:9.5 v/v). When Co²⁺-**4a** (1:1) adduct with absorption maxima at 308 nm and 388 nm was treated with (Bu)₄NF a significant bathochromic shift ($\Delta\lambda_{\text{max}} = 95$ nm) of the absorption at 388 nm was observed with the appearance of a new absorption peak at 483 nm (Fig. 4). This fluoride binding was observed to be accompanied by a prominent 'naked eye' colour change from light yellow to dark purple. Similarly when **4a**-F⁻ (1:1) complex with absorption maxima at 287 and 483 nm was treated with Co(ClO₄)₂ solution, λ_{max} at 287 nm shifted to 308 nm. Appearance of similar UV-visible spectral change and colorimetric behaviour indicates that **4a** simultaneously and quantitatively recognises Co²⁺ and F⁻ ions at appropriate binding sites.

When experiments were repeated with other synthesized receptors (**4b**, **4c** and **4d**), their λ_{max} values were found to exhibit similar bathochromic shifts when same concentrations of Co²⁺ and F⁻ ions were added to their solution (Table S1, Supplementary data). However it was determined that the cation binding sites on the ditopic receptors were prone to interference with silver and copper ions. For example, under identical conditions, when one equivalent of Ag⁺ was treated with 20 μM solution of **4a** in DMSO:CH₃CN (0.5:9.5 v/v), the absorption band at 287 nm was shifted to 307 nm, while no shift in the absorption peak at 388 nm (fluoride binding sites) was observed. Gradual addition of fluoride ions to 1:1 molar ratio of **4a**-Ag⁺ complex solution resulted in the displacement of silver ions which caused the disappearance of the absorption peak at 307 nm and the regeneration of the original absorption peak at 287 nm but no shift in the

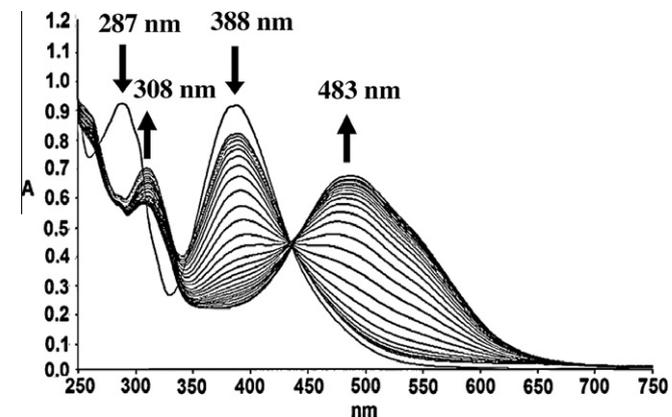


Figure 4. Titration curve of compound **6a**, Co(II) (1:1) upon addition of tetrabutylammonium fluoride (0–100 equiv) in DMSO/CH₃CN (1:9 v/v).

absorption peak at 388 nm until the addition of more than one equivalent of fluoride ion. Further addition of tetrabutylammonium fluoride exhibited a bathochromic shift of maximum at 388 nm to 483 nm with a distinct 'naked eye' colour change from light yellow to dark purple.

The above observations clearly indicate that the addition of the first equivalent of fluoride ion may lead to the sequestering of the metal ion to form a stable ion pair with fluoride ion in solution which effectively inhibits the anion binding with the receptor molecule as reported earlier.¹⁴ However, when the sequestering of metal ion gets completed, further addition of fluoride leads to the enhancement in intensity of the 483 nm peak plausibly due to the complexation of fluoride ion as expected. Similar results were obtained when titration of **4a** was performed with fluoride ion in the presence of one equivalent of Cu²⁺ ion.

In conclusion, we have synthesized and characterized novel ditopic calix[4]arene based receptors **4a–d** that possess both hydrazone and bipyridyl functions at the lower rim. The synthesized molecular receptors have been determined to recognize Co²⁺ and fluoride ions simultaneously. They exhibit a substantial bathochromic shift to elicit a distinct 'naked eye' colour change for fluoride ions. However, it was determined that Ag⁺ and Cu²⁺ ions interfere in the binding of fluoride ion with **4a**.

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Supplementary data

Supplementary data (synthetic procedures, characterisation data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.02.083.

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