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ORIGINAL ARTICLE

Evaluation of deep cavity imidazolylcalix[n]arenes for selective extraction of silver

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Abstract A series of diphenylimidazolyl calix[n]arenes ($n = 4, 6, 8$) obtained from readily available starting materials have been examined for selective extraction of monovalent (sodium, potassium, caesium and silver) and bivalent ions (barium and lead). It has been determined that the synthesized deep cavity imidazolyl calix[n]arenes can selectively recognize silver ions through interaction with the imidazolyl groups appended at their upper rim in contrast to their usually encountered complexation with the ester functionalities present at the lower rim. The silver extraction efficiency is limited in the absence of the calix[n]arene skeleton while it is radically influenced by the ring size of imidazolylcalix[n]arenes examined.

Keywords Imidazolylcalixarenes · Deep cavity · Cone conformation · Extraction · Silver ions

Introduction

Recognition of metal ions of biological [1, 2], medicinal [3, 4], radioactive [5, 6] and environmental significance [7] is an area of intense research activity [8, 9]. Owing to the presence of distinct hydrophobic and hydrophilic regions and adjustable cavity dimensions in their molecular architecture, calixarenes have attracted considerable attention for the design of useful receptors [10–18]. By functionally modifying either the hydrophobic region (upper rim) or hydrophilic region (lower rim), it is possible to obtain efficient host molecules for complexing cations [11, 12, 19–22], anions [23–25] and neutral species [26–28]. The ionophoric nature of calixarenes has also been explored by us [29–32] earlier. It has been determined that some substituted calixarenes assist in the liquid–liquid extraction of alkali metal picrates into dichloromethane [33]. Thus *p-tert*-butylcalix[n]arenes ($n = 4, 6, 8$) possessing -$CH_2COOC_2H_5$ groups show significant ion selectivities as compared to parent *p-tert*-butylcalix[n]arenes ($n = 4, 6, 8$) [34] when examined under the same experimental conditions. The selectivities exhibited by specific calixarene esters were strongly dependent on the size of the ions extracted [35]. The electron-withdrawing groups on the upper rim of the calix[4]arene scaffold has also been found to assert a negative effect on the absolute amount of metal ions extracted with a higher selectivity towards sodium cations [36]. X-ray crystal structures of the dinuclear complexes of 1, 3-alternate calix[4]arene-bis(crown-6) with thallium picrate, rubidium picrate and cesium picrate have been reported [37]. The structural data in solution and the solid state has revealed that the π-coordination of monovalent thalium ion with the calixarene aromatic framework plays an important role in the enhanced complexing ability of the calix-biscrown compounds towards thallous ions. Similar detailed experiments have revealed that some organic guest molecules are also held deeply and tightly in the aromatic cavity of calixarenes plausibly due to CH–π interactions [38–40].

It has also been observed that calixarenes undergo a change in conformation when subjected to complexation with metal ions or on formation of inclusion compounds. Reinhoudt et al. [41] have described that the 1,3-alternate

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conformer of calixarene crowns has a high complexing ability for cesium picrate than other conformers of the same molecular scaffold. There has also been a considerable interest in the utilization of other calixarene based three dimensional structures for the purpose of molecular recognition.

Though considerable efforts have been made in recent years to elaborate calix[n]arenes at the upper or lower rim to achieve the stated purpose [18, 42–44], studies related to the formation of deep and wide cavity calixarenes, [45–47] have been limited. In this context, the imidazole ring system can function both as a proton acceptor and a donor and can mimic enzyme functions in certain situations while under other conditions it can act as a metal ion [48–50] or anion [51] complexant. The attachment of imidazole units with calixarenes without any spacer unit would be expected to function as efficient receptors suitable for metal ions or organic molecules to result in modified reactivities. In order to examine this possibility, we decided to couple the imidazole and calixarene units to generate molecular scaffolds for selective binding which might lead to the construction of molecular devices. It was also envisioned that direct introduction of imidazole rings at para positions of the calixarene framework would provide deeper and wider cavity calixarenes with greater hydrophilicity for encapsulation of larger ions and molecules. Recently, our group has synthesized a series of cone configured *p*-imidazolyl-calix[n]arenes (*n* = 4, 6, 8) by a five step synthetic methodology (Fig. 1) [22]. We now report evaluation of synthesized calixarenes for binding metal ion picrates through extraction experiments, UV–Vis and inductively coupled plasma atomic emission spectroscopies. Specific interactions between *p*-imidazolyl calix[n]arenes and metal ions have also been studied by NMR spectroscopy.

Results and discussion

Metal ion extraction when attempted according to the method described by Lein and Cram [52] showed that imidazolyl calix[n]arenes are better extractants of metal ion picrates as compared to the debutylated methoxy calixarenes **2a**, and **2b** (Fig. 2).

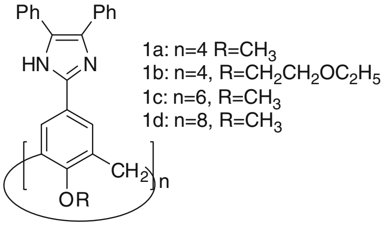
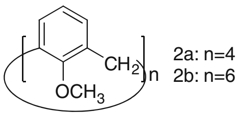


Fig. 1 Structure of *p*-imidazolylcalix[n]arenes **1a–d**

Fig. 2 Stucture of methoxy derivatives of calix[n]arenes



For example, *p*-(4,5-diphenylimidazol-2-yl)calix[n]arenes **1a** and **1c** showed pronounced extraction capabilities (94 and 53%, respectively) for silver picrate in comparison to other picrates of monovalent ions (lithium, potassium, cesium) and bivalent cations (calcium and barium) which showed weaker extraction capabilities (less than 15%). Since **1a** was found to be an excellent extractant for silver ion from amongst other ions, detailed studies as presented here were majorly carried out on extraction of silver ions. For example, a solid complex (**1a**-silver picrate) was isolated by slow evaporation of a mixed solution of **1a** (1×10^{-3} M) and silver picrate (1×10^{-3} M). The residue obtained though could not provide a single crystal suitable for X-ray determination; it gave significant information when subjected to the ^{1}H-NMR spectroscopic analysis. It has been determined that the imidazole N–H signal at δ14.9 disappears on treatment with silver ions indicating the presence of strong NH···metal ion interactions. Likewise, a considerable shift in the position of aromatic protons of calixarenes (δ 7.32–7.16) and sharpening of signals for aromatic protons of the phenyl moiety could be observed which indicated that the silver ion was binding at the upper rim cavity of imidazolyl calix[4]arenes when present in their cone conformation. No change in the chemical shifts was observed for the protons of the lower rim functionalities on complexation with silver ions. Research groups led by Shinkai [53, 54] and Reinhoudt [55] have also inferred similar results from their observations on differently substituted calixarenes.

p-Imidazolylcalix[n]arenes as metal ion extractants: UV–Visible spectroscopic studies

When chloroform solution of the *p*-imidazolylcalix[n]arene was shaken with an aqueous solution of the metal picrate at 298 K for 3 h, the metal ion picrate could be extracted into the chloroform layer. Since the metal picrates were insoluble in chloroform, the amount of metal picrate present in the chloroform layer after liquid–liquid extraction implied that the *p*-imidazolylcalix[n]arene host had extracted it from the aqueous to the chloroform layer. This was marked by a decrease in the metal picrate concentration in the aqueous layer. The concentration range of picrate extraction was determined by examining the effectivity of the Beer Lambert Law to the system. An aliquot of the aqueous solution was withdrawn and its UV spectrum was recorded.

A similar blank extraction was performed in the absence of the calixarene host. The extractability was determined by measuring the absorbance of picrate ion ($\lambda_{\max} = 354$ nm) in the aqueous solutions by means of Eq. 1:

$$\%E = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where, A_0 = Absorbance of the aqueous layer of the blank reaction at $\lambda_{\max}$, 354 nm, A = Absorbance of the aqueous layer of the reaction with the calixarene host at $\lambda_{\max}$, 354 nm.

Through utilization of this method, it was estimated that **1a**, **1b** and **1d** showed excellent extractability for silver picrate (94, 99.7 and 98.6%, respectively) as compared to the other metal ion picrates, while **1c** exhibited moderate extractability for silver (53%). The percentage extraction of the other metal picrates by the calix[8]arene derivative **1d** was found to be higher than that observed for the corresponding calix[4]arene derivatives **1a** and **1b** (Fig. 3).

It was observed that the percentage extraction of sodium, potassium and cesium picrates by calix[4]arene derivatives **1a** and **1b** was very similar while calix[8]arene derivative **1d** extracted sodium picrate to a greater extent as compared to potassium and the cesium picrates. From amongst the bivalent metal picrates, calcium and lead picrates were found to be extracted to a greater extent than barium picrate by the calix[8]arene derivative **1d** as compared to the corresponding calix[4]arene derivatives **1a** and **1b** which did not evince significant discrimination in their extraction behaviour towards bivalent metal picrates.

p-Imidazolylcalix[n]arenes as selective metal extractants: Inductively coupled plasma atomic emission spectroscopic experiments

To determine the selectivity (if any) of calixarenes **1b** and **1d** for metal ion extraction, an equimolar mixture of sodium, potassium, cesium and silver picrates were taken in water and stirred with a chloroform solution of the host molecule **1b** or **1d** for 3 h. A blank experiment with the same composition of the metal picrates but without host molecules was also carried out simultaneously. The aqueous layer was separated and the concentration of each metal ion was determined by inductively coupled plasma atomic emission spectroscopy (ICPAES). The percentage extraction of metal ion picrates was calculated by employing the equation.

$$\%E = \frac{c_0 - c}{c_0} \times 100 \tag{2}$$

Where, c_0= Concentration of the metal ion in the aqueous layer of the blank reaction, c = Concentration of the metal ion in the aqueous layer of the reaction with the calixarene host.

As can be seen from Fig. 4, both the imidazolylcalix[n]arene **1b** and **1d**, exhibited a high selectivity for silver ion when it was present in association with other metal ions.

It should be noted that there were marked differences in the selectivity traits of **1b** and **1d**. For instance, potassium was extracted with almost equal preference to sodium by **1b** while sodium was extracted more than potassium by **1d** (50.8–3.0%). ICPAES analysis failed to detect any extracted cesium within the studied experimental concentration range (≤200 ppm).

Stoichiometry of *p*-imidazolylcalix[n]arene-silver complexes

From the previous discussion, it is evident that *p*-imidazolyl calixarenes can serve as excellent extractants for silver ions. Consequently, further studies were carried out to examine the nature of silver-imidazolyl calixarene interaction. A series of liquid–liquid extraction experiments were carried out by varying the concentration of both the

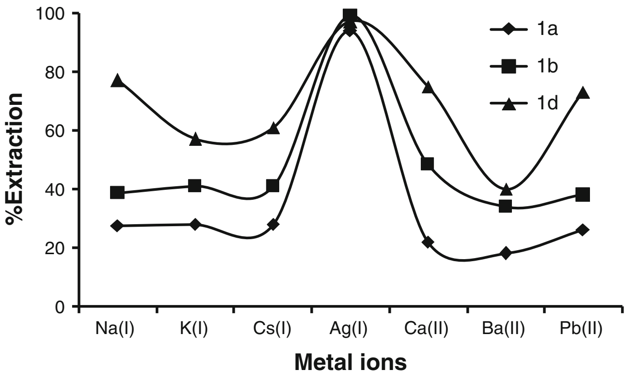


Fig. 3 Percentage extraction of metal picrates (1×10^{-3} M) by ligands **1a**, **1b** and **1d** (5×10^{-4} M) from water to chloroform layer

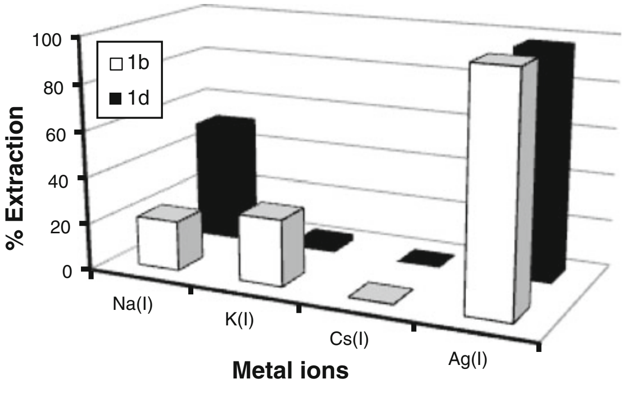


Fig. 4 Percentage extraction of individual metal picrate from a mixture of metal ion picrates (1×10^{-3} M each) by **1b** and **1d** (5×10^{-4} M), respectively

metal (silver picrate) and the calixarene derivative (**1b**) in such a way that the total number of moles of silver picrate and that of the calixarene ligand **1b** remained constant ($X_M + X_L = 1.0$ mmol). Stoichiometry of the complex formed was determined by utilizing Eq. 6 which was derived as follows [56]:

$$[\mathrm{M}^+]_a + [\mathrm{Pic}^-]_a + q[\mathrm{H}]_o \overset{K}{\leftrightarrows} \{\mathrm{M}^+\mathrm{Pic}^-q[\mathrm{H}]\}_o \quad (3)$$

$$K = \frac{\{\mathrm{M}^+\mathrm{Pic}^-q[\mathrm{H}]\}_o}{[\mathrm{M}^+]_a[\mathrm{Pic}^-]_a\{[\mathrm{H}]_o\}^q} \quad (4)$$

where, Eq. 3 expresses the extraction equilibrium, Eq. 4 expresses the extraction constant K

The subscripts a and o denote the aqueous and organic phases, respectively and 'H' and 'pic$^-$' denote the host (calixarene) molecule and the picrate anion, respectively.

The *p*-imidazolyl calixarene ligand and the complex $\{\mathrm{M}^+\mathrm{pic}^-q[\mathrm{H}]\}_o$ are highly lipophilic and do not dissolve in the aqueous phase. Therefore, the concentration of the complex in the organic phase was considered to be equivalent to the picrate ion concentration in the organic phase which in turn was assumed to be equal to the picrate ion concentration extracted from the aqueous phase into the organic phase.

The distribution ratio (D) could thus be expressed as given in Eq. 5

$$D = \frac{\{\mathrm{M}^+\mathrm{Pic}^-q[\mathrm{H}]\}_o}{[\mathrm{M}^+]_a} \quad (5)$$

In a logarithmic form, Eqs. 4 and 5 can be represented by Eq. 6,

$$\log D/[\mathrm{Pic}^-]_a = \log K + q \log [\mathrm{H}]_o \quad (6)$$

Equation (6) leads to a straight line in which the slope gives the value of *q*. When this equation was applied to observations made in the case of imidazolyl calixarene **1b**, it gave a plot of log $D/[\mathrm{Pic}]_a$ against log $[\mathbf{1b}]_o$ as a straight line with slope equal to 0.88 (Fig. 5a). This revealed that the stoichiometry of **1b**: silver picrate complex is 1:1, i.e., 1 M of **1b** complexes with 1 M of silver.

Similar concentration dependent extraction studies on silver picrate in case of *p*-imidazolylcalix[8]arene **1d** (Fig. 5b) showed it to complex with silver in a 1:2 fashion, i.e., for every host molecule (**1d**), there were two silver ions associated with it.

Attempts at structural elucidation of *p*-imidazolylcalix[n]arene-silver complexes

(a) Ultra-violet spectroscopic evidence

The chloroform layer containing the imidazolylcalixarene-metal picrate complex obtained in the extraction experiments was separated from the aqueous layer and its UV–Visible spectrum were recorded and analyzed for any shifts in their absorption maxima. For instance, the spectral change of **1b** after silver picrate extraction is given in Fig. 6, where curves **a** and **b** represent the UV–Vis spectrum of **1b** before and after complexation. The spectral analysis indicated that the shift in λ_{max} of **1b** is not very substantial (303–298 nm) but there was a concomitant appearance of new peaks at 419 and 367 nm. Similar spectral changes were also observed for **1d**.

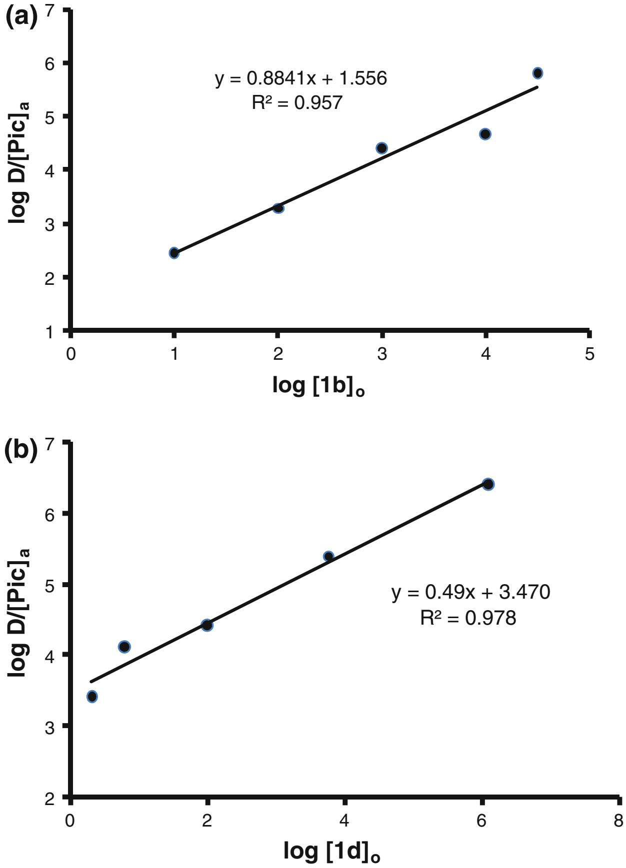


Fig. 5 Plot of **a** log $D/[\mathrm{pic}]_a$ vs. log $[\mathbf{1b}]_o$ **b** log $D/[\mathrm{pic}]_a$ vs. log $[\mathbf{1d}]_o$

(b) Nuclear magnetic resonance spectroscopic evidence

A comparison of the ^{1}H-NMR spectra of **1b** with that of the silver complex of **1b** (Fig. 7) revealed that significant changes occurred during this interaction as depicted in Table 1. The two sets of multiplets and the singlet observed for the protons on the phenyl rings of the imidazolyl moiety and the *m*-protons of the central calix[4]arene framework gave way to a complicated series of multiplets in the aromatic region. However, the pair of doublets ($\mathrm{ArC\underline{H}_2Ar}$), the two triplets ($\mathrm{-OC\underline{H}_2}$, $\mathrm{C\underline{H}_2O-}$) and the quartet ($\mathrm{-OC\underline{H}_2CH_3}$) observed in the NMR spectrum of **1b** did not show any changes in the chemical shifts (Table 1).

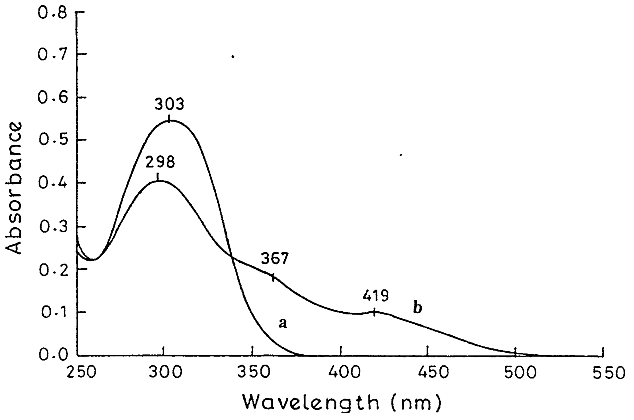


Fig. 6 UV–Vis spectrum of **1b** **a** before and **b** after silver picrate extraction

This strongly suggested that silver ions are probably interacting with **1b** through the upper rim rather than the lower rim. The signal observed at δ8.66 could be due to the aromatic protons of the picric acid.

Role of imidazolyl-NH on extraction of silver picrate

p-Imidazolylcalix[n]arenes **1b** and **1d** ($n = 4$, 8) were converted to the corresponding *N*-alkylated derivatives, *p*-imidazolylcalix[n]arenes **3a** and **3b,** by treatment with 2-bromoethyl acetate in the presence of sodium hydride as the base in DMF at room temperature (Scheme 1). Compounds **3a** and 3**b** were evaluated for their silver picrate extraction efficiency in separate experiments using the same liquid–liquid extraction protocol as described for **1b** and **1d**. The percentage extraction of silver picrate by **3a** and **3b** (Table 2) was found to be the same, thereby suggesting that the hydrogen attached to the nitrogen of the imidazole ring does not take part in the complexation process.

Effect of calixarene macrocyclic σ-framework on the extraction of silver picrate

Since imidazoles have high affinity for metal ions and are known to complex several transition metal ions, it was necessary to see whether recognition of silver ions was selective indeed. It was therefore considered important to determine whether recognition is due to the macrocyclic nature of *p*-imidazolylcalixarene or simply due to the presence of the imidazole units. Consequently, experiments were designed to delineate the role of the cyclic framework of calix[n]arenes by synthesizing a non-cyclic analog of imidazolylcalixarenes by refluxing *p*-anisaldehyde with benzil in the presence of excess of ammonium acetate in acetic acid to obtain 2-(4′-methoxyphenyl)-4,5-diphenylimidazole **4** (Scheme 2).

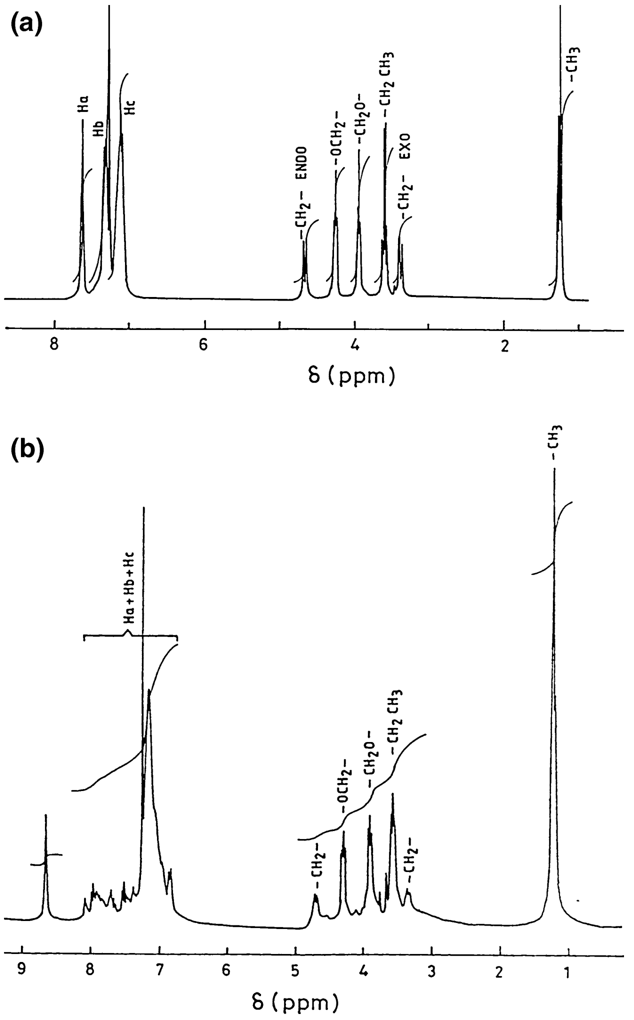
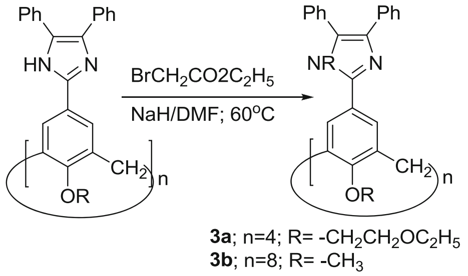


Fig. 7 ^{1}H-NMR spectrum of **a** **1b**, **b** **1b**–silver picrate complex in $CDCl_3$ at 25 °C

Table 1 Comparison of the ^{1}H-NMR spectral pattern of **1b** and its silver complex

Compound	$CDCl_3$, δ, ppm	
	Aromatic region	Aliphatic region
1b	7.32–7.30 (m), 7.15–6.90 (m) 7.62 (s)	4.46 (d), 4.26 (t), 3.94 (t), 3.60 (q), 3.36 (d), 1.26 (t)
1b-Silver complex	8.15–6.8 (m)	4.43 (d), 4.26 (t), 3.94 (t), 3.57 (q), 3.38 (d), 1.24 (t)

Similar extraction studies were carried out with **4** by taking different concentrations (1, 4 and 8 mM) for extraction of the silver picrate (1 mM). Since **1b** had four and **1d** had eight imidazole appendages, the extraction efficiency was expected to be equivalent to four and eight molecules of **4** if the macrocyclic σ-framework was ignored. It was found that even with an eight fold excess of molar equivalents of **4,** there was a maximum of only 60.3% of the amount of silver



Scheme 1 Synthesis of N-(ethoxycarbonylmethoxy)imidazolylcalix[n]arenes **3a**,**b**

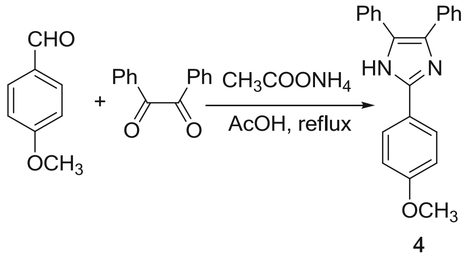
Table 2 Percentage extraction of silver picrate (1×10^{-3} M) **1b**, **1d**, **3a** and **3b** (5×10^{-4} M each)

Mpic	1b	3a	1d	3b
Agpic	99.8	97.3	98.6	96.5

picrate extracted by the imidazolylcalixarenes (Fig. 8). This extraction efficiency is much lower than that extracted (>98%) by the imidazolylcalix[n]arenes. Since imidazolylcalix[4]arenes and imidazolylcalix[6]arenes could extract the silver picrate almost to a similar extent and the number of moles of silver picrate extracted with imidazolylcalix[8]arene were almost double of that of imidazolylcalix[4]arene, it could be inferred that the former compound is functioning as if it were constituted of two units of imidazolylcalix[4]arenes. This indicated that the size and nature of the macrocyclic structure of calixarene has a major role to play in the silver ion recognition process. Further work to identify the exact nature of interactions and the influence of a specific conformation on extraction efficiency for sliver is in progress and will be reported in due course.

Experimental

All the starting materials were purchased from Merck and Sigma-Aldrich and were used without further purification. The solvents used were purified and dried before use by recommended procedures [*"Purifications of Laboratory Chemicals" by W. L. F. Armarego and D. D. Perrin, Bath Press, Bath, Britain*].



Scheme 2 Synthesis of 2-(4′-methoxyphenyl)-4,5-diphenyl imidazole, **4**

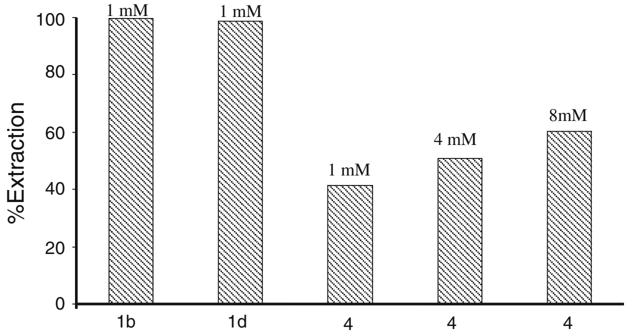


Fig. 8 % Extraction of silver picrate by **1b**, **1d** and their acyclic analog, **4** at different concentrations

The melting points reported in this paper are uncorrected and were taken on an electric melting point apparatus (Toshniwal, India). UV spectra were recorded on Hitachi 330 and Perkin Elmer (Lambda-3B) spectrophotometers. IR spectra were recorded in KBr discs on a [5-DX] Nicolet FT-IR and Nicolet protégé 460 ESP spectrophotometers while NMR spectra were recorded on Bruker 300 MHz NMR machine using TMS as internal standard and the values reported are on the δ scale. FAB-Mass spectra were recorded on a Jeol SX 103/DA-6000 mass spectrometer at Sophisticated Analytical Instrumenta Facility (SAIF) at Central Drug Research Institute (CDRI), Lucknow. Molecular weights were determined by using vapour pressure osmometer (Knauer, Germany). Elemental analysis has been carried on a Perkin Elmer 240C-CHN analyzer.

Synthesis of deployed *p*-imidazolylcalix[n]arenes

p-Tert-butylcalix[4,6 and 8]arenes, calix[n]arenes, calix[n]arene aldehydes and imidazolyl calix[n]arenes were synthesized by the methods reported in the literature [29]. Debutylation was carried out by using $AlCl_3$/phenol/toluene as reported by Gutsche while calixarene aldehydes were made by the methods reported earlier from our labs. The synthesized compounds were purified through crystallization and column chromatography over silica gel (60 mesh, BDH chemicals) and were fully characterized by comparison of their physical and chromatographic data with that of the authentic samples as well as their chemical derivatization (mainly acetylation and benzoylation reactions). The purity of compounds used for extraction studies was checked on TLC before proceeding further on deployment of extraction protocols reported in this paper.

Extraction behaviour of synthesized imidazolyl calix[4]arenes

The ionophoric behaviour of imidazolylcalixarenes was evaluated by two phase extraction methodology. The interaction of synthesized imidazolyl calixarenes with metal ions was determined through UV–Vis spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICPAES), and NMR measurements. The synthesized *p*-imidazolylcalix[n]arenes were examined as molecular hosts for sodium, potassium, cesium, silver, calcium, barium and lead picrates, prepared by reported procedures from carbonates (cesium, silver, barium, and lead), acetates (sodium and potassium) and calcium chloride and hot aqueous picric acid. The cation binding properties of the synthesized *p*-imidazolylcalix[n]arenes were explored by the liquid–liquid extraction [52].

*Synthesis of 5,11,17,23-tetrakis-{4′,5′-diphenyl-(N-ethoxycarbonylmethoxy)imidazolyl} -25,26,27,28-tetrakis(2-ethoxyethoxy) calix[4]arene **3a***

A solution of 5,11,17,23-tetrakis(4′,5′-diphenyl)imidazolyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (0.1 g, 0.06 mmol) in DMF (10 mL) was treated with NaH (0.02 g, 0.8 mmol) till effervescence ceased. 2-Bromoethyl acetate (0.1 g, 0.6 mmol) was added to it and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was poured into ice cold water (50 mL) and the solid residue was obtained by filtration. It was dissolved in chloroform, washed with dil. HCl (1%, 2 × 20 mL) and subsequently with water (2 × 25 mL). The organic extract was dried (Na_2SO_4) and evaporated under vacuum to yield a solid which was recrystallized from chloroform–methanol (2:1) to yield **3a** as a pale yellow powder. Yield: 0.071 g, 61%, m.p. > 250 °C; Anal. calcd. for $C_{120}H_{120}O_{16}N_8$: C, 74.68; H, 6.22; N, 5.80; found: C, 74.38; H, 6.59; N, 5.61; Molecular mass (vapour pressure osmometry): 1,943 (Calcd. 1,928); UV (λ_{max}, $CHCl_3$): 284 nm; IR (ν_{max}, KBr): 1,756, 1,596, 1,500, 1,488, 1,435, 1,386, 1,211, 1,148, 768 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.33–7.31 (m, 16H, Ar$\underline{H}$), 7.16–6.92 (m, 24H, Ar′$\underline{H}$), 7.65(s, 8H, Ar$\underline{H}$), 4.46 (d, 4H, J = 13.1 Hz, ArC$\underline{H}_2$Ar), 4.29 (m, 16H, –C$\underline{H}_2$), 3.95–3.91 (m, 20H, –C$\underline{H}_2$), 3.61 (m, 8H, ArC$\underline{H}_2$Ar, –CH_2), 1.29–1.25 (m, 24H, –C$\underline{H}_3$).

*Synthesis of 5,11,17,23,29,35,41,47-octakis{4′,5′-diphenyl-(N-ethoxycarbonylmethoxy)-imidazolyl}-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene **3b***

A solution of **1d** (0.22 g, 0.08 mmol) in DMF (15 mL) was treated with NaH (0.04 g, 0.016 mmol) till effervescence ceased. Immediately afterwards, 2-bromoethyl acetate (0.26 g, 1.6 mmol) was added to the reaction mixture and the whole mass was stirred at room temperature for 24 h. The reaction mixture was poured into ice cold water (75 mL) and the solid residue was obtained by filtration. It was dissolved in chloroform, washed with dil. HCl (1%, 2 × 25 mL) followed by washing with water (2 × 25 mL), and the organic extract was dried (Na_2SO_4) and evaporated under vacuum. The solid obtained was recrystallized from chloroform–hexane (1:2) to give **3b** as a pale yellow powder (0.18 g, 68.4%); m.p. 228–230 °C; Anal. calcd. for $C_{216}H_{192}H_{24}N_{16}$: C, 76.53; H, 5.42; N, 6.01; found: C, 76.84; H, 5:33; N, 5.88; Molecular mass (vapour pressure osmometry) 3,410 (Calcd. 3,392); UV (λ_{max}, $CHCl_3$): 290 nm; IR (ν_{max},, KBr): 1,754, 1,595, 1,508, 1,475, 1,428, 1,381, 1,302, 1,272, 1,210, 765 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.44–7.38 (m, 32H, Ar′$\underline{H}$), 7.15-7.11 (m, 48H, Ar′$\underline{H}$), 7.83 (s, 16H, Ar$\underline{H}$), 4.28(s, 16H, –C$\underline{H}_2$), 4.09 (s, 16H, ArC$\underline{H}_2$Ar), 3.75 (q, 16H, J = 7.0 Hz, –C$\underline{H}_2$), 3.55 (s, 24H, OC$\underline{H}_3$), 1.33 (t, 24H, J = 7.0 Hz, –C$\underline{H}_3$).

*Synthesis of 4,5-diphenyl-2(4′-methoxyphenyl)imidazole **4***

A solution of benzil (5.25 g, 25 mmol) and *p*-anisaldehyde (3.40 g, 25 mmol) in glacial acetic acid (50 mL) was treated with ammonium acetate (10 g, 130 mmol). After refluxing the solution for 2.5 h, the reaction mixture was poured into crushed ice (200 g) and the precipitate obtained after 1 h was collected by filtration under suction. On recrystallization from hot methanol, it gave compound **4** (6.23 g, 77%) as pale yellow needles. m.p. 225 °C; Anal. calcd. for $C_{22}H_{18}N_2O$; C, 80.98; H, 5.52; N, 8.59; found: C, 81.00; H, 5.51; N, 8.57; IR (ν_{max}, KBr): 3,300, 1,605, 1,589, 1,496, 1,360, 1,288, 1,055, 788, 645 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.76 (d, 2H, J = 6.9 Hz, Ar$\underline{H}$), 7.58–7.48 (m, 4H, Ar′$\underline{H}$), 7.38–7.28 (m, 6H, Ar′$\underline{H}$), 6.98 (d, J = 6.9 Hz, 2H, Ar$\underline{H}$), 3.84 (s, 3H, OC$\underline{H}_3$).

General procedure for the preparation of metal picrates

The metal picrates (sodium, potassium, cesium, silver, calcium, barium, lead) were obtained from hot aqueous solution of picric acid in the presence of excess metal salt. While $CH_3COONa\cdot 3H_2O$ was used for the preparation of sodium picrate, metal carbonates were used for obtaining potassium, cesium, silver and calcium picrates. Barium and lead nitrates were used for obtaining barium and lead picrates. The mixed hot solution was allowed to cool after filtering (the undissolved particles in case of carbonates) and allowed to stand until precipitation was complete. The obtained metal picrates were dried under vacuum and were protected from moisture and light before use.

The synthesized metal picrates were characterized by their IR spectra and melting points. While the formation of metal picrates and their purity was strongly indicated by the absence of strong absorption at 3,105 cm^{-1} (due to

-OH of picric acid) in their IR spectra, their melting points were also found to be much higher (>250 °C) as compared to picric acid (114 °C). Fresh metal picrate solutions were prepared every time the experiments were repeated (Note: picric acid and metal picrates are sensitive explosives).

Picric acid, m.p. 112–114 °C; IR (ν_{max}, KBr): 3,105, 1,633, 1,609, 1,527, 1,432, 1,343, 1,176, 1,153, 1,088, 919, 832, 783.

Sodium picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,635, 1,560, 1,516, 1,496, 1,435, 1,371, 1,336, 1,278, 1,163, 908.

Potassium picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,631, 1,562, 1,493, 1,436, 1,368, 1,330, 1,277, 1,168, 907.

Cesium picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,635, 1,559, 1,490, 1,431, 1,374, 1,332, 1,274, 1,168, 908.

Silver picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,638, 1,559, 1,489, 1,432, 1,370, 1,332, 1,273, 1,167, 912.

Calcium picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,630, 1,558, 1,485, 1,432, 1,367, 1,331, 1,271, 1,166, 908.

Barium picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,632, 1,559, 1,488, 1,435, 1,369, 1,333, 1,270, 1,168, 910.

Lead picrate, m.p. > 250 °C; IR (ν_{max}, KBr): 1,630, 1,559, 1,483, 1,435, 1,368, 1,330, 1,271, 1,165, 908.

General procedure for the preparation of stock solution of metal picrate

For the preparation of 1×10^{-2} M solution of metal picrates, the required amount of metal picrate was accurately weighed and dissolved in water (10 mL) in a 100 mL standard flask. Water was added up to the mark.

General procedure for the preparation of ligand solution

For the preparation of 1×10^{-3} M solution of ligand, the required amount of ligand was accurately weighed and dissolved in (10 mL) chloroform in a 50 mL standard flask. The volume was made up to the mark by addition of chloroform. The prepared stock solutions were diluted as per the required concentration in a particular experiment.

UV spectrophotometric analysis

Extraction procedure

In a typical experiment, an aqueous metal picrate solution (5 mL, 1×10^{-3} M) and a chloroform solution of ligand (5 mL, 5×10^{-4} M) were taken in a stoppered flask and the mixed solutions were magnetically stirred for 3 h at room temperature after which the phases were allowed to separate. The chloroform and the aqueous phases were separated by means of a separatory funnel. The absorbance "A" of the aqueous layer was recorded at λ, 354 nm (dilution of the aqueous layer was quantitatively done to bring the absorbance within the instrumental range). A blank experiment without calixarene derivative was run under the same conditions and absorbance 'A_0' of the aqueous solution was measured at λ, 354 nm. The percentage of metal ion extracted was calculated as the ratio $100 \times \frac{A_0 - A}{A_0}$.

UV–Vis studies for determination of stoichiometry of 5b-silver complex

The stoichiometry was determined by examining the effect of continuous variation of concentration of both the calix[4]arene ligand and that of the silver picrate solution. A series of solutions of **1b** in chloroform (1.0, 2.0, 3.0, 4.0 and 4.5 mM) and, a series of silver picrate solutions (0.5, 1.0, 2.0, 3.0 and 4.0 mM) in distilled water were prepared. Extraction experiments were set-up in which 5 mL of the chloroform solution was mixed with 5 mL silver picrate solution in such a way that the sum of total concentration of both the ligand (**1b**) and metal ion (silver ion) was constant i.e., $c_L + c_M =$ constant (5×10^{-3} mM). The absorbance (A_0 and A) of picrate anion in the aqueous layer at 354 mM was then determined.

From the concentration and absorbance values, log $D/[pic]_a$ and $\log[H]_o$ were calculated and incorporated into Eq. 6 to calculate the stoichiometry of the **1b**-silver complex. Similar experiments were set-up to determine the stoichiometry of the **1d**-silver complex.

UV–Vis studies to explore the role of cyclic framework

Similar concentration dependent extraction studies as discussed in the earlier section were repeated with the non-cyclic analog **4** (5 mL) at three different concentrations, i.e., 1, 4 and 8 mM. The ligand solution was separately stirred with 1 mM of silver picrate (5 mL) and the % extraction of metal picrate in the aqueous layer was calculated.

Selectivity traits of **1b** and **1d** as ionophores by inductively coupled plasma atomic emission spectroscopy

Aqueous metal picrate solutions (sodium picrate, potassium picrate, cesium picrate and silver picrate) (10 mL, 4×10^{-3} M) were mixed together in a 100 mL round bottomed flask and chloroform solution of ligand (**1b** or **1d**) (40 mL, 5×10^{-4} M) was added to it. The two solutions were mixed and stirred for 3 h at 25 °C. A parallel blank experiment without imidazolyl calixarene host was carried out under identical conditions. The aqueous layers in both the cases were taken for inductivity coupled plasma atomic emission spectroscopic analysis which directly measured the concentration of each metal ions (in ppm). For such ICPAES analysis, initially a series of standard solutions of each metal picrates were made and were fed into the instrument to give a standard calibration curve for the corresponding metal ion. Concentration 'c' of the particular metal ion was measured along with the concentration of the metal ion in the blank experiment 'c_o' in the aqueous layer. Percentage extraction of that particular metal ion was calculated using the equation

$$c_o - \frac{c}{c_o} \times 100.$$

*Isolation of p-imidazolylcalix[4]arene **1a**-silver complex*

Slow evaporation of chloroform solution containing **1a**-silver picrate gave a yellow coloured solid which was recrystallized from hot methanol as pale yellow complex. m.p. 332 °C (decomp.); IR (KBr, ν_{max}): 2,100, 1,610, 1,598, 1,540, 1,453, 1,380, 1,310, 1,262, 1,200, 1,193, 1,110, 1,085, 960, 778, 650 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 8.01–7.58 (m, 4H, $Ar\underline{H}$), 6.87 (s, 8H, $Ar\underline{H}$), 4.03 (d, 4H, $J = 12$ Hz, $ArC\underline{H}_2Ar$), 3.51 (s, 12H, $-OC\underline{H}_3$), 3.40 (d, 4H, $J = 12$ Hz, $ArC\underline{H}_2Ar$).

*Isolation of p-imidazolylcalix[4]arene **1b**-silver complex*

Slow evaporation of a chloroform solution containing *p*-imidazolylcalix[4]arene **1b**-silver picrate gave yellow needle shaped crystals. The crystals were not suitable for X-ray analysis. M.p. > 250 °C; IR (KBr, ν_{max}): 2,963, 2,926, 1,715, 1,558, 1,449, 1,362, 1,261, 1,097, 1,097, 1,020, 801 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 8.66 (s, 4H, $Ar''\underline{H}$), 8.02–7.15 (m, 48H, $Ar\underline{H}$ and $Ar'\underline{H}$), 4.43 (d, 4H, $ArC\underline{H}_2Ar$), 4.26 (t, 8H, $-OC\underline{H}_2$), 3.94 (t, 8H, $C\underline{H}_2O$), 3.57 (q, 8H, $-C\underline{H}CH_3$), 3.38 (d, 4H, $ArC\underline{H}_2Ar$), 1.24 (t, 12H, $-CH_2C\underline{H}_3$).

*Isolation of p-imidazolylcalix[8]arene **1d**-silver complex*

Slow evaporation of a chloroform solution of complex *p*-imidazolylcalix[8]arene **1d**-silver picrate gave a yellow solid. m.p. > 250 °C; IR (ν_{max}, KBr): 2,965, 2,355, 1,693, 1,613, 1,560, 1,450, 1,261, 1,095, 1,016, 802 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 8.64 (s, 8H, $Ar''\underline{H}$), 7.93–7.21 (m, 96H, $Ar\underline{H}$ and $Ar'\underline{H}$), 4.09 (s, 16H, $ArC\underline{H}_2Ar$), 3.58 (s, 24H, $-OC\underline{H}_3$).

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