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Synthesis and application of an efficient calix[4]arene-based anion receptor bearing imidazole groups for Cr(VI) anionic species

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ABSTRACT

We synthesized the new calix[4]arene amines bearing two and four imidazole or *tert*-butylamine moieties (**9a**,**b**/**10a**,**b**) by the reaction of di- or tetra-tosylated calix[4]arene derivatives (**7** and **8**, respectively) with 1-(3-aminopropyl)imidazole and/or *tert*-butylamine, respectively. After the characterization of **9a**,**b**/**10a**,**b** their extraction abilities toward Cr(VI) anionic species (CAS) was evaluated and compared by the liquid–liquid extraction method. The extraction results revealed that calix[4]arene amine having four imidazole groups (**10a**) was an efficient anion receptor for CAS. Moreover, the extraction of CAS by **10a** in the presence of other anions such as Cl^-, NO_3^-, and PO_4^{3-} showed that **10a** could be a selective anion receptor for CAS in the presence of those anions.

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1. Introduction

Deterioration of water quality due to the presence of toxic heavy metals in environmental water resources introduced by industrial pollution is a serious matter of concern today.[1] Chromium (Cr) is one of the most commonly present heavy metal pollutants in industrial wastewater. In aqueous solution Cr is found in two stable oxidation states; trivalent and hexavalent. Cr(VI) is widely used in electroplating, leather tanning, metal finishing, photography, dye and textile industries. The effluents from these industries often contain elevated levels of Cr(VI). Cr(III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid, and protein metabolism. Cr(VI) can be toxic as it can diffuse as $Cr_2O_7^{2-}$ or $HCr_2O_7^-$ through cell membranes and oxidize biological molecules. So, human contact with Cr(VI) is known to cause severe health problems such as skin irritation, liver damage, pulmonary congestion, vomiting, and ulceration.[2,3] As a result, the treatment of wastewater containing Cr(VI) prior to discharge is essential. Several methods, such as liquid–liquid extraction, adsorption, chemical precipitation, membrane separation, evaporation, and electrochemical treatment have been used to remove these Cr(VI) anionic species (CAS) from aqueous solutions. Among them, liquid–liquid extraction is the most common system for the removal of these anions. This needs efficient anion receptors.

Design of anion receptors for such applications remains a great challenge for chemists because they have to take into consideration the specific anion properties, such as a large range of shapes and geometries, small electric charges versus sizes, high free energies of solvation and, in some cases, multiple oxidation states of the central atoms in anions or pH dependence.[4] In many artificial anion hosts, noncovalent interactions are responsible for host–guest recognition. They include electrostatic interactions, hydrogen bonding, hydrophobic effects, and coordination to a metal ion or combinations of these interactions. The hosts can be neutral, containing urea,[5–8] thiourea,[9,10] or amide[11] functions. They can also be positively charged, containing pyridinium,[12] polyammonium,[13] or quaternary ammonium[14] binding sites.

Calixarenes[15] are often used as scaffolds onto which these functional groups can be attached. They are well-known macrocyclic compounds that have been studied extensively for host–guest chemistry.[15] They can be readily functionalized through the phenolic groups or directly on the aromatic ring and this has resulted in the design and synthesis of a variety of derivatives for a wide range of functions. One of the more widely studied areas of calixarene chemistry is their use as ionophores for both cations and anions.[16–18] This has resulted in applications in ion selective electrodes,[19,20] metal extraction,[21–23] and catalysis.[24,25] Recently, various amide, amine, and pyridinium-functionalized calixarenes, which interact with anions via electrostatic interactions or hydrogen bonding have been reported as anion receptors.[26–29] We anticipated that attaching the appropriate groups to increase these interactions would be

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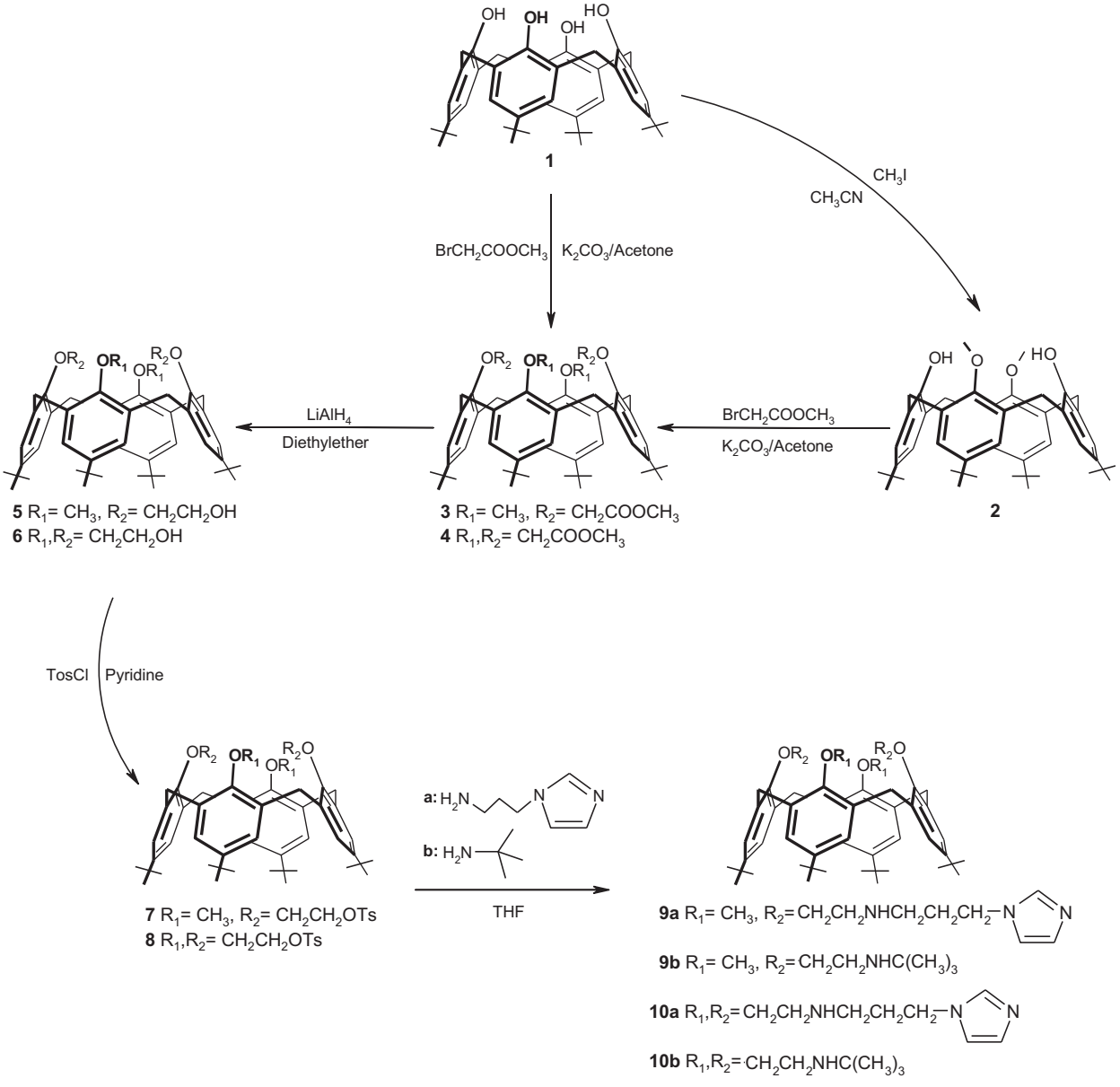
good strategy for the synthesis of efficient calix[4]arene-based anion receptors for CAS. As such, we decided to introduce 'imidazole' onto an amino calix[4]arene framework as a substituent[30] due to it having two additional nitrogen atoms for these interactions. Consequently, in the current work we considered that calix[4]arene amines bearing imidazole groups would be more effective ligands than the previously studied ones for the extraction of CAS. To evaluate this approach, we initially synthesized and characterized imidazole-substituted calix[4]arene amines (Scheme 1) and then examined their extraction abilities toward CAS.

2. Results and discussion

2.1. Synthesis

We were interested in the synthesis of calix[4]arene-based ligands having imidazole binding sites (**9a** and **10a**) in order to evaluate their complexation abilities toward CAS such as $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ through the liquid–liquid extraction system. The *tert*-butyl amine analogs (**9b** and **10b**) were also synthesized to compare their extraction properties for CAS with those of the imidazole-substituted ones. The synthesis of **1**–**8** and **9a**,**b**–**10a**,**b** was conducted as shown in Scheme 1.

Compounds **1**–**8** were synthesized according to previously literature methods[15,31] and then their structures confirmed in this study. After the preparation of **7** and **8**, they were reacted with 2.05 or 4.1 equiv of 1-(3-aminopropyl)imidazole and *tert*-butylamine in dry THF at room temperature for 5 h to obtain **9a**, **9b**, **10a**, and **10b** in 68%, 52%, 64%, and 49% yields, respectively. The new compounds have been characterized by a combination of ^{1}H NMR, FTIR, FABMS, and elemental analysis. The FTIR spectra of **9a**,**b** and **10a**,**b** show amine bands at 3148 cm^{-1}, 3142 cm^{-1}, 3147 cm^{-1}, and 3143 cm^{-1}, respectively. Following the 'De Mendoza rule',[32] compounds **9a**,**b** and **10b** were confirmed to be present in the *cone* conformation by detailed study of their ^{1}H NMR spectra (doublets at 3.32 ppm, 4.27 ppm, J=13.1, at 3.32 ppm, 4.28 ppm, J=13.1 Hz and at 3.00 ppm, 4.22 ppm, J=12.8 Hz for ArCH$_2$Ar protons, respectively). The conformation of **10a** could not be determined due to the peaks,



Scheme 1. The synthetic steps for the preparation of calix[4]arene amines **9a**,**b**/**10a**,**b**.

which belong to its $ArCH_2Ar$ protons overlapping with those of other $-CH_2-$ protons. On the other hand, the singlets at 1.42, 1.18, and 1.15 ppm for −NH− protons of **9a**,**b** and **10a** (it was overlapped at the range of 1.45–1.15 for **10b**), and the multiplets in the range of 7.40–7.18 and 7.80–6.50 ppm for imidazole protons of **9a** and **10a**, respectively, in their ^1H NMR spectra were some of the peaks proving the substitution.

2.2. Extraction studies

In this study, liquid–liquid extraction experiments were performed to examine the extraction behavior of CAS such as $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ from the aqueous phase into the organic phase (dichloromethane) by using the new calix[4]arene amine derivatives **9a**,**b** and **10a**,**b** at the range of pH 1.5–4.5. The equilibrium concentration of CAS in aqueous phase was determined spectrophotometrically. The extraction experiments with imidazole-substituted calix[4]arenes (**9a** and **10a**) at pH 1.5–2.5 could not be performed because of their water solubility at those pH values.

From the results presented in Table 1, it has been observed that the imidazole-substituted calix[4]arene amine derivatives **9a** and **10a** (especially **10a**) are found to be effective extractants for the phase transfer of CAS at pH 3.5–4.5. However, it has been clearly demonstrated that an increase in the pH there is a decrease in extraction ratios for all ligands. This can be explained by the fact that the ligands contain 'proton-switchable' binding sites, appropriate for the achieving CAS at low pHs. That is, it has been indicated that the partially protonated forms of ligands are effective hosts for CAS. Upon addition of NaOH to the aqueous layer, the deprotonated calixarenes in the dichloromethane are no longer an effective host molecule for CAS, and the monoanion migrates back into the aqueous layer in a reversible process (Scheme 2). This is in agreement with the literature[27] where the extraction of CAS with a calix[4]arene derivative occurs when the aqueous phase is only acidic especially at low pH values so that it leads to form the proton ligands. This is a particularly important feature if it is desirable to recover the metal in pure form and reuse the extractant by changing the pH of aqueous solution.[27]

Table 1
The extraction percentages (±0.1) of CAS by the calix[4]arene amines[a]

Ligand	pH			
	1.5	2.5	3.5	4.5
9a	—[b]	—[b]	64.2	23.1
9b	15.1	8.36	2.14	0
10a	—[b]	—[b]	90.2	84.8
10b	14.0	0	0	0

[a] Aqueous phase, $[Na_2Cr_2O_7]=1.0\times10^{-4}$ M; organic phase, dichloromethane, [ligand]$=1.0\times10^{-3}$ M, at 25 °C, for 1 h.
[b] Could not be performed due to water solubility in this pH.

Importantly, according to the best of our knowledge, the extraction results by **10a** indicate that CAS can be extracted for the first time in this study in quite high yields (approximately 90%) even at pH 3.5. This can be attributed to calix[4]arene amine bearing tetra-imidazole parts has more proton-switchable units when it is compared to previously reported calix[4]arene amine-based CAS receptors although some of them was not used as a ligand under same extraction conditions.[27–29] On the other hand, from the extraction results it is also observed that the *tert*-butylamine-bonded calix[4]arenes are less effective ligands than their imidazole-bonded analogs even at low pHs. This can be described by steric hindrance of the flexible and bulky *tert*-butyl groups of **9b** and **10b**. Besides, the lower CAS extraction of **10b** than that of **9b** supports this explanation due to the **10b** has more *tert*-butyl groups than **9b**. It must be clarified that the combination of steric effects, hydrogen binding, and electrostatic interactions between calix[4]arene amines and CAS are major factors in the complexation process. Consequently, it is revealed that our claim in the beginning of this study to get more efficient ligands than those of the previously published ones for the CAS extraction by calix[4]arene amines is a good approach.

To gain a deeper insight into the complexation process, the extraction data were also analyzed by using the classical slope analysis method. Assuming the extraction of an anion (A) by the anion receptor (L) according to the following equilibrium:

$$n(L)_{org} + n(A)_{aq} \rightleftharpoons \left((L)_n, (A)_n\right)_{org} \quad (1)$$

The extraction constant K_{ex} is then defined by:

$$K_{ex} = \frac{\left[\left((L)_n, (A)_n\right)\right]_{org}}{[A]^n_{aq}[L]^n_{org}} \quad (2)$$

Eq. 2 can be re-written as:

$$\log D_A = \log K_{ex} + n \log[L]_{org} \quad (3)$$

where D_A is defined as ratio of the analytical concentration of the anion (A) in both phases:

$$D_A = [A]_{org}/[A]_{aq} \quad (4)$$

A plot of the $\log D_A$ versus log[L] may lead to a straight line whose slope allows to access the stoichiometry of the extracted species. Fig. 1 represents the extraction into dichloromethane at different concentrations of **10a** for CAS. A linear relationship between log *D* versus log[L] is observed with a slope for CAS by **10a**, which equals 0.94 at pH 3.5 suggesting that **10a** form 1:1 complex with CAS (Scheme 2).

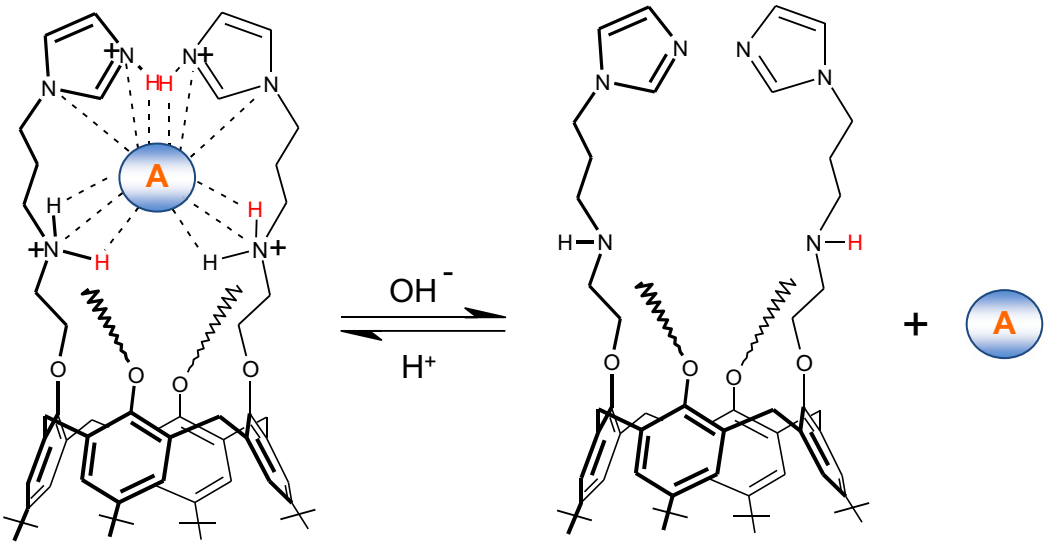
However, it is well-known that at more acidic conditions $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$, and after ionization in an aqueous solution it exists in the $HCr_2O_7^-/Cr_2O_7^{2-}$ form.[27] This allowed us to consider these simultaneous extractions of 1:1 complexes according to the following equilibria (Eq. 5). According to these assumptions, the extraction constant (K_{ex}) has been calculated from the experimental data. The calculation of this constant value lead to log K_{ex} (±0.2)=3.60 for **10a**.

$$LH^{n+}_{n(org)} + HCr_2O_7^-/Cr_2O_{7(ag)}^{2-} \rightleftharpoons \left[LH^{n+}_n, \left(HCr_2O_7^-/Cr_2O_7^{2-}\right)\right]_{org} \quad (L = \mathbf{10a}) \quad (5)$$

Moreover, in order to understand the selectivity of CAS extraction by **10a** in the presence of competitive anions the extraction studies were also carried out using the sodium salts of different anions such as Cl^-, NO_3^- and PO_4^{3-}, and their mixtures. The results summarized in Table 2 indicate that the extraction of CAS by **10a** is not affected by the presence of these anions. This implied that the removal of CAS in liquid–liquid extraction system by **10a** can be almost selective in the presence of these selected anions.

3. Conclusions

In this study, new calix[4]arene amine derivatives bearing imidazole and *tert*-butyl amine groups were synthesized and characterized, and their extraction behavior was evaluated and compared by the liquid–liquid extraction method for CAS. The results showed that the extraction of CAS by tetraamine-derivatized calix[4]arene **10a** having imidazole moieties mostly took place in quite high yield (90%) and was greater than its corresponding *tert*-butyl amine-derivatized analogs **9b** and **10b** (negligible extraction for both of them) and also diimidazole-substituted derivative **9a**



Scheme 2. The proposed interactions of compound **10a** with CAS (A: $HCr_2O_7^-$, $Cr_2O_7^{2-}$, only two imidazole binding sites are represented for clarity).

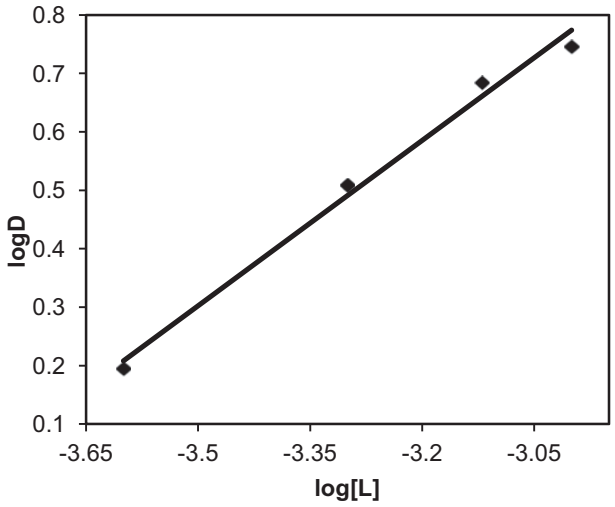


Fig. 1. Log *D* versus log[L] for the extraction of CAS by the ligand **10a** from an aqueous phase into dichloromethane at 25 °C and pH 3.5.

Table 2
The CAS extraction results (±0.1) by **10a** in the presence of competitive anions (Cl^-, NO_3^-, and PO_4^{3-}) and their mixtures[a]

Ligand	Added anion[b]	Extracted CAS (%)
10a	—	90.2
	Cl^-	85.4
	PO_4^{3-}	89.8
	NO_3^-	87.7
	Cl^-, PO_4^{3-}, and NO_3^-	84.6

[a] $[Na_2Cr_2O_7]=1.0\times10^{-4}$ M; [**10a**]$=1.0\times10^{-3}$ M, at 25 °C, pH 3.5.
[b] The concentration of competitive anions$=1.0\times10^{-3}$ M.

(64%) at pH 3.5. Additionally, the selectivity experiments demonstrated the extraction of CAS by **10a** was not affected by the presence of some selected anions such as Cl^-, NO_3^-, and PO_4^{3-} and their mixtures even they used more concentrated than the concentration of CAS. Consequently, we reported that an efficient and selective calix[4]arene-based anion receptor (**10a**) bearing proton-switchable units for CAS.

4. Experimental section

4.1. General

Melting points were determined using an Electrothermal 9100 apparatus in a sealed capillary and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as the internal standard. FTIR spectra were obtained on a Perkin–Elmer Spectrum 100 FTIR spectrometer. UV–visible spectra were obtained on PG Instruments T80+ UV–visible recording spectrophotometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. FABMS spectra were taken on a Varian MAT 312 spectrometer. An Orion 420A pH meter was used for the pH measurements. Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). The chromatographic separations were performed on a Merck Silica Gel 60 (230–400 mesh). All reactions were conducted under nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Sigma–Aldrich, and used without further purification. The commercial grade solvents were distilled and stored over molecular sieves. The drying agent employed was anhydrous sodium sulfate. Anions were used as their sodium salts in the extraction studies. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

4.2. Synthesis of anion receptors

Scheme 1 illustrates the successive synthetic steps of the several amino calix[4]arenes and their precursors (**1**–**8**, **9a**, **9b**, **10a**, and **10b**). Compounds **1**–**8** were prepared following or by adapting to previously published procedures.[15,31] In current work, compounds **9a**,**b** and **10a**,**b** were firstly synthesized according to our knowledge.

The preparation of compounds **9a**,**b** and **10a**,**b** is carried out as following the general procedure: 1-(3-aminopropyl)imidazole or *tert*-butylamine (2.05 or 4.10 mmol) was added to a solution of **7**/**8** (1.00 mmol) dissolved in dry THF (20 mL), respectively. After the mixture was stirred at room temperature for 5 h, distilled water (10 mL) was added to the solution. The mixture was extracted with dichloromethane, washed with distilled water (2×50 mL), brine (2×50 mL), and then dried over anhydrous sodium sulfate. The

solvent was evaporated under vacuo, and recrystallized from dichloromethane to give **9a**,**b**/**10a**,**b** as white crystals.

*4.2.1. 5,11,17,23-Tetra-tert-butyl-25,27-di-[1-(3-aminopropylethoxy) imidazolyl]-26,28-dimethoxycalix[4]arene (**9a**).* Yield: 68%; mp: 158 °C. FTIR: 3148 cm^{-1} (NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40–7.18 (m, 6H, $H_{imidazole}$); 7.06 (s, 4H, Ar*H*); 6.75 (s, 4H, Ar*H*); 4.27 (d, *J*=13.1 Hz, 4H, ArCH_2Ar); 3.94 (br s, 8H, OCH_2CH_2N); 3.90–3.60 (m, 10H, OCH_3, NHCH$_2$CH$_2$CH_2N); 3.32 (d, *J*=13.1 Hz, 4H, ArCH_2Ar); 2.43 (br s, 4H, NHCH_2CH$_2$CH$_2$N); 1.84 (m, 4H, NHCH$_2$CH_2CH$_2$N); 1.42 (s, 2H, N*H*); 1.29 (s, 18H, (CH_3)$_3$C); 0.92 (s, 18H, (CH_3)$_3$C). FABMS *m*/*z*: 1002.21 $(M+Na)^+$. Anal. calcd for $C_{62}H_{86}N_6O_4$ (979.38): C, 76.03; H, 8.85; N, 8.58. Found: C, 75.98; H, 8.80; N, 8.56.

*4.2.2. 5,11,17,23-Tetra-tert-butyl-25,27-di-(tert-butylaminoethoxy)-26,28-dimethoxycalix[4]-arene (**9b**).* Yield: 52%; mp: 142 °C. FTIR: 3142 cm^{-1} (NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.06 (s, 4H, Ar*H*); 6.75 (s, 4H, Ar*H*); 4.28 (d, *J*=13.1 Hz, 4H, ArCH_2Ar); 3.94 (br s, 8H, OCH_2CH_2N); 3.85–3.65 (m, 6H, OCH_3); 3.32 (d, *J*=13.0 Hz, 4H, ArCH_2Ar); 1.30 (br s, 36H, (CH_3)$_3$C-NH, (CH_3)$_3$C-Ar); 1.18 (br s, 2H, N*H*); 0.92 (s, 18H, (CH_3)$_3$C-Ar). FABMS *m*/*z*: 898.12 $(M+Na)^+$. Anal. calcd for $C_{58}H_{86}N_2O_4$ (875.31): C, 79.59; H, 9.90; N, 3.20. Found: C, 79.58; H, 9.88; N, 3.19.

*4.2.3. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-[1-(3-aminopropylethoxy)imidazolyl]-calix[4]arene (**10a**).* Yield: 64%; mp: 169 °C. FTIR: 3147 cm^{-1} (NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80–6.50 (m, 20H, Ar*H*, $H_{imidazole}$); 4.40–3.30 (m, 32H, ArCH_2Ar, NHCH$_2$CH$_2$CH_2N, OCH_2CH_2N); 2.90 (br s, 8H, NHCH_2CH$_2$CH$_2$N); 1.94 (br s, 8H, NHCH$_2$CH_2CH$_2$N); 1.15 (s, 4H, N*H*); 1.05 (s, 36H, (CH_3)$_3$C). FABMS *m*/*z*: 1276.55 $(M+Na)^+$. Anal. calcd for $C_{76}H_{108}N_{12}O_4$ (1253.74): C, 72.81; H, 8.68; N, 13.41. Found: C, 72.88; H, 8.72; N, 13.42.

*4.2.4. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-(tert-butylaminoethoxy)calix[4]arene (**10b**).* Yield: 49%; mp: 157 °C. FTIR: 3143 cm^{-1} (NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.70 (s, 8H, Ar*H*); 4.39 (br s, 8H, OCH_2CH$_2$N); 4.22 (d, *J*=12.8 Hz, 4H, ArCH_2Ar); 4.09 (br s, 8H, OCH$_2$CH_2N); 3.00 (d, *J*=12.8 Hz, 4H, ArCH_2Ar); 2.43 (s, 18H, (CH_3)$_3$C-NH); 1.45–1.15 (m, 22H, N*H*, (CH_3)$_3$C-NH); 1.05 (s, 36H, (CH_3)$_3$C-Ar). FABMS *m*/*z*: 1068.40 $(M+Na)^+$. Anal. calcd for $C_{68}H_{108}N_4O_4$ (1045.61): C, 78.11; H, 10.41; N, 5.36. Found: C, 78.18; H, 10.45; N, 5.37.

4.3. Liquid–liquid extraction studies

The anion extraction experiments by the calix[4]arene amine derivatives (**9a**,**b** and **10a**,**b**) were performed following Pedersen's procedure.[33] An aqueous solution of sodium salt of anion (10 mL of a 1.0×10^{-4} M; 0.01 M KOH/HCl solution was used in order to obtain the desired pH at equilibrium) and calixarene ligand (10 mL of 1.0×10^{-3} M) in dichloromethane were shaken vigorously in a stoppered glass tube with a mechanical shaker for 2 min and then magnetically stirred in a thermostated water bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of anion remaining in the aqueous phase was then determined as described previously for CAS.[26] Blank experiments showed that no CAS extraction occurred in the absence of calix[4]arene derivatives. The percent extraction (*E*%) was calculated from the absorbance *A* of the aqueous phase measured at 350 nm (for pH 1.5–4.5) using the following expression:

$$E\% = [(A_0 - A/A_0)] \times 100 \quad (6)$$

where A_o and *A* are the initial and final concentrations of the CAS before and after the extraction, respectively.

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