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ORIGINAL ARTICLE

Synthesis of two new *p-tert*-butylcalix[4]arene *β*-ketoimin derivatives for extraction of dichromate anion

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Abstract In this study the selective derivatization of *p-tert*-butylcalix[4]arene was carried out and two new *p-tert*-butylcalix[4]arene *β*-ketoimin, 5,11,17,23-tetra-*tert*-butyl-25,27-bis-3-methyl-[(*β*-ketoimine)-ethoxy]-26,28-dihydroxycalix[4]arene (**4**), and 5,11,17,23-tetra-*tert*-butyl-25,27-bis-3-chloro-[(*β*-ketoimine)-ethoxy]-26,28-dihydroxycalix[4]arene (**5**) have been synthesized. In the synthesis, the lower rim of *p-tert*-butylcalix[4]arene was modified in order to acquire binding site for the recognition of dichromate anion. It was observed that these ionophores **4** and **5** showed high affinity towards dichromate anion. The protonated Schiff-base forms of the receptors were effective for transferring the $HCr_2O_7^-$ anion from aqueous phase to a dichloromethane phase.

Keywords Calixarene · *β*-Ketoimine · Transition metal · Alkali metal · Liquid–liquid extraction

Introduction

The importance of calixarenes has been entirely recognized since pioneering studies of Gutsche [1–4]. This can be largely attributed to the fact that they are attractive host molecules that can be easily functionalized into suitable binding sites for target guest species [5]. Calixarenes are cyclic oligomers made of several phenolic units bounded with methylene bridges. The phenolic-OH of the calixarenes lower rim can be further functionalized to give various ionic receptors [6, 7]. The introduction of two or four different groups as ester [8, 9], keto and amide [10–12] on the phenolic-OH groups of calixarenes fixes this macrocycle in the "cone" structure giving metal selective cation receptors [13–16]. Selective calixarene-based receptors for cations and neutral molecules [17–21] have been synthesized in the past decade.

Selective signaling of heavy metal ions is a very important topic for the detection and treatment of the toxic metal ions in various chemical systems. In this field, calixarenes are useful ionic receptors due to potential functionalization possibilities. On the other hand the attachment of binding groups at the lower rim allows the coordination of different metal ions with high selectivity. Ester and amide derivatives of calix[4]arenes in the cone conformation bind sodium and calcium ions very strongly, whereas calix[4]arene-crown ethers in 1,3-alternate conformation are very selective towards cesium [22], depending on the ring size. The molecular recognition of anionic guest species by positively charged or electron deficient neutral abiotic receptor molecules are an area of intense current interest. The importance of favorable amine, amide, or imide hydrogen bonding interactions for anion binding has recently been exploited in the design of calix[4]arene anion receptors, although such host molecules are still relatively rare. In the recent years, we have reported that calix[4]arene-based receptors effectively bind anion. This feature can be useful for multiple applications such as laboratory, clinical, environmental and industrial process analyses [23, 24].

Although several works [25, 26] regarding the synthesis and complexation of metal cations with calix[4]arene ketoimine derivatives have been reported, no work has been published for their complexion with oxyanions.

We now synthesized two new calix[4]arene platform with *β*-ketoimine derivatives on their lower rim as

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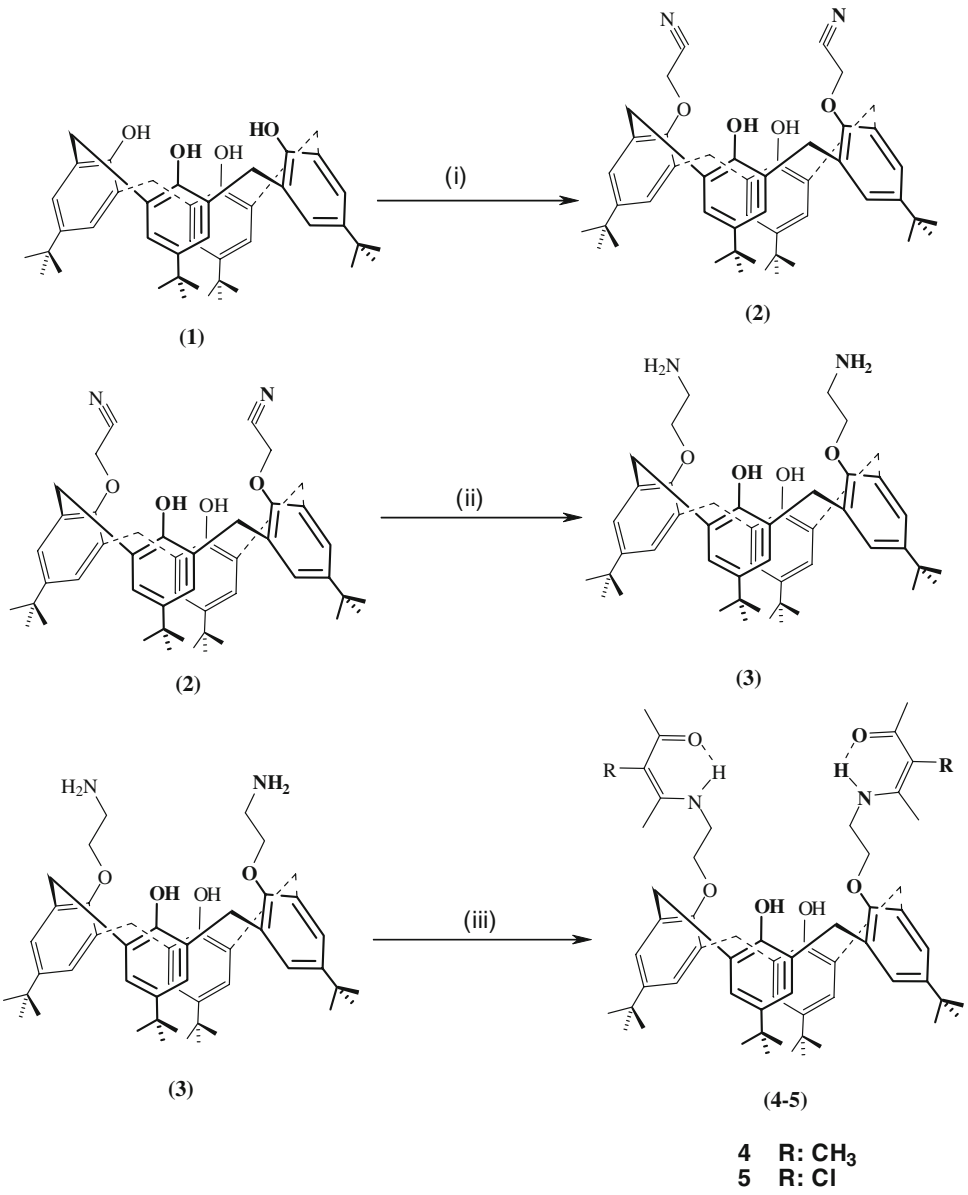
mentioned in Scheme 1 and investigated their ligating behavior by means of liquid–liquid phase sorption of dichromate anions from aqueous solution.

Results and discussion

Synthesis

The synthetic course of new type β-ketoimine groups at the lower rim of *p-tert*-butylcalix[4]arene derivatives is given in Scheme 1. For the synthesis of *p-tert*-butylcalix[4]-arenes based on β-ketoimine derivatives, the parent compounds **1–3** were prepared according to published procedures [27–29]. All of the structures have been characterized through ^{1}H NMR, IR, and Elemental analyses. We are interested in the synthesis of *p-tert*-butylcalix[4]arene-based ionophores having β-ketoimine binding sites in order to investigate their binding ability toward dichromate anions in two-phase solvent extraction systems. Compounds **4** and **5** contain β-ketoimine moieties in their structures, and therefore they may provide an effective binding site for chromate ions in highly acidic media. Our motive behind the synthesis of these type calixarene derivatives was to examine their possible applications in anion-binding processes; we do believe that these calixarene derivatives can successively be used in separation of small quantities of potentially harmful solute, anions. *p-tert*-Butylcalix[4]arene β-ketoimine derivatives (**4** and **5**) have been prepared in three steps as shown in Scheme 1. Firstly, *p-tert*-butylcalix[4]arene



Scheme 1 Schematic illustration of β-ketoimine *p-tert*-butylcalix[4]arene derivatives. (i) K_2CO_3/CH_3CN, $BrCH_2CN$, reflux; (ii) $LiAlH_4$, $C_2H_5OC_2H_5$, reflux and C_6H_6/H_2O; (iii) $CH_3COCHCH_3COCH_3$ or $CH_3COCHClCOCH_3$, CH_2Cl_2/C_2H_5OH, reflux

was functionalized with nitrile groups by *o*-substitution on the lower rim of calix[4]arene in distal position. The treatment of *p-tert*-butylcalix[4]arene with bromoacetonitrile in the presence of K_2CO_3 in dry acetonitrile gave the di-substituted nitrile compound **2**. Compound **2** was then reduced into the corresponding amine derivative **3**. Finally the amine calixarene derivative was treated with 3-methyl-pentan-2,4-dione or 3-chloro-pentan-2,4-dione in a mixture of ethanol/dichloromethane in the presence of molecular sieves in order to trap water molecules to give the corresponding p-*tert*-butylcalix[4]arene β-ketoimine derivatives (**4** and **5**). All of the structures were in cone conformation in solution as proved by the appearance of $ArCH_2Ar$ which displays a typical AB type proton signal at 3.20–4.20 ppm (J = 13.0–13.6 Hz) respectively. This situation is confirmed by the ^{1}H NMR spectra. The high field doublets at 3.28 ppm for **4** and 3.24 ppm for **5** are assigned to the equatorial protons of methylene groups, whereas the low field signals at 4.20 ppm for **4** and 4.21 ppm for **5** are assigned to the axial protons in the ^{1}H NMR spectra. Furthermore, the β-ketoimine groups are characterized by the presence of three singlet peaks at 1.94, 2.12 and 2.27 ppm for the methyl groups in compound **4** and two singlet peaks around 1.90 and 2.15 ppm for the compound **5**. On the other hand, the presence of new one triplet peak around the 11 ppm is attributable to NH proton of compounds **4** and **5**. This chemical shift of NH proton is deshielded probably as a result of the formation of an intramolecular hydrogen bond as mentioned in literature [30]. Furthermore, in the ^{1}H NMR data of compounds **4** and **5** two singlet peaks attributable to *tert*-butyl groups are observed around 0.88 and 1.29–1.32 ppm and triplet peaks attributable to aliphatic protons (CH_2CH_2) are also observed around 3.80 and 4.10 ppm. It is stated that the number of protons obtained from ^{1}H NMR data is equal to the number in the proposed structure of the compounds (**4** and **5**).

In the previous study, x-ray analysis of a β-ketoimine derivative of *p-tert*-butylcalix[4]arene β-ketoimine from the condensation of the amino calix[4]-arene with acetylacetone, was obtained. It was observed that the structure of compound shows the intermolecular hydrogen bonds concerning the phenolic proton. Moreover the β-ketoimine group shows two kinds of interactions: the two NH groups form intramolecular and intermolecular hydrogen bonds with the CO group of the same macrocycle and one CO group of the neighboring one. So this structure shows a very interesting packing with strong intermolecular interactions along the axis of polymeric chain.

Two-phase solvent extractions

The removal of the dichromate anions from water sources gained high attention because of their high toxicallity affect. For a molecule to be effective as a host, it is necessary that its structural features are compatible with those of the guest anions. The dichromate ions ($Cr_2O_7^{2-}$/$HCr_2O_7^-$) are anions where the periphery of the anion has oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. It is known that calix[4]arenes with a nitrogen functionality such as pyridine, amino, and imino on their lower rim are efficient extractants for oxoanions [31–33]. For this purpose, we have designed extractants (**4** and **5**) having proton-switchable binding lobes for anions. We have performed some preliminary evaluations to investigate binding efficiencies of the extractants **4** and **5** for $Na_2Cr_2O_7$ by using solvent extraction. The results showed that $Na_2Cr_2O_7$ could be extracted from aqueous solution into dichloromethane at different pH values. The results were summarized in Fig. 1.

An aqueous solution of $Na_2Cr_2O_7$ showed no extraction into an organic phase in the absence of the extractant. *p-tert*-Butylcalix[4]arene β-ketoimine derivatives (**4** and **5**) provided suitable binding sites for the dichromate anions at low pH due to the presence of protonable amine moieties. At the lower pH values both the formation of $NaHCr_2O_7^-$ and the protonation of the amine nitrogens favors extraction into dichloromethane. Since the free energy of hydration of the alkylammonium ion is less than that of the sodium ion, the extracted complex will be primarily the alkylammonium salt of **4** and **5** with $HCr_2O_7^-$. Therefore, an anion-switchable complex is formed in the two-phase extraction system. Upon addition of NaOH to the aqueous layer, the deprotonated calixarene in the CH_2Cl_2 is no longer an effective host molecule for $Cr_2O_7^{2-}$ and the dianion then migrates back into the aqueous layer in a

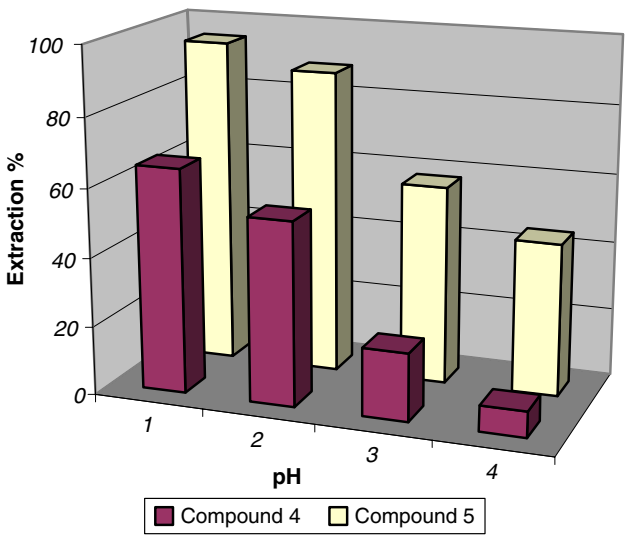


Fig. 1 Anion extraction yields obtained on synthesized ligands for different pH. (H_2O/CH_2Cl_2: 10/10 (v/v); Sodium dichromate 1×10^{-4} M; Ligand: 1.10^{-3} M, 1 H. 25°C)

reversible process as shown in Scheme 2. This situation results from the proton transfer to the nitrogen atom of the amine unit in compounds **4** and **5**. In aqueous solutions having a lower pH the dichromate will be primarily in its protonated form $HCr_2O_7^-$. This monoanion will have a smaller free energy of hydration compared to dianionic form $Cr_2O_7^{2-}$. As a result, there is a smaller loss in hydration energy as $HCr_2O_7^-$ is transferred from the aqueous phase into the dichloromethane phase. An additional advantage of $HCr_2O_7^-$ over $Cr_2O_7^{2-}$ is that for the former only one sodium ion needs to be coextracted to maintain charge balance, whereas for $Cr_2O_7^{2-}$ two sodium ions are extracted, with additional loss of hydration energy [34]. From the extraction data given in Fig. 1, it is clear that both the extractants **4** and **5** are more effective for the extraction of dichromate anions at low pH. This is not a surprising result because extractants **4** and **5** contain appropriate proton switchable amine group binding sites for aggregation of anions at low pH. Moreover, from the results in different pH values, it was clearly understood that compound **5** is better extractants than compound **4** for dichromate anions as shown in Fig. 1. All data have been analyzed using the classical slope analysis method [35]. Assuming that the extraction of an anion A^{n-} by the receptor LH^{n+} is according to following equilibrium:

$$n(LH^{n+})_{org} + nA^{n-}_{aq} \rightleftharpoons [(LH^{n+})_{n,}A^{n-}_{n}]_{org} \quad (1)$$

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

$$K_{ex} = \frac{[((LH^{n+})_{n,}A^{n-}_{n})]_{org}}{[A^{n-}]^{n}_{aq}[LH^{n+}]^{n}_{org}} \quad (2)$$

Eq. 2 can be re-written as;

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

where D_A is defined as the ratio of the analytical concentration of the anion A^{n-} in both phases:

$$D_A = [A]_{org}/[A]_{aq}$$

Consequently a plot of the log D_A versus log [*L*] may lead to a straight line with a [*L*]slope that allows for the determination of the stoichiometry of the extracted species, which is defined as the analytical concentration of the ligand in the organic phase. Figure 2 exhibits the extraction into dichloromethane at different concentrations of **4** and **5** with dichromate, respectively. A linear relationship between log D_A versus log [*L*] is observed with the slope of the line for extraction of dichromate anion by ligands **4** and **5** is approximately equal to 1.07 (for ligand **4** and for ligand **5** at pH 1.5, respectively), suggesting that these ligands **4** and **5** form 1:1 complexes with the dichromate anion. 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. At higher acidic conditions $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr^{6+} form and p*Ka1* and p*Ka2* values of these equations are 0.74 and 6.49, respectively. It is clear that the ligands **4** and **5** form complex mostly with $HCr_2O_7^-$ ion. This has allowed us to consider that mostly the Eq. 4 is simultaneous extraction of 1:1 complexes according to the following equilibria:

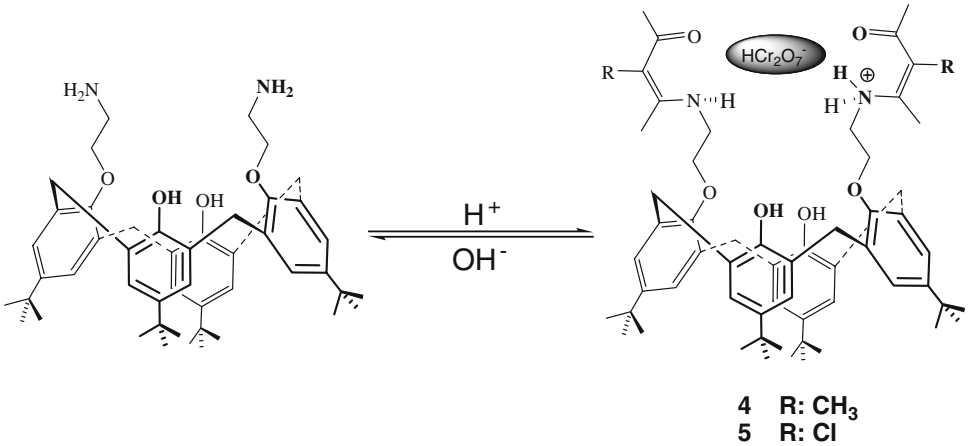
$$(LH)^{+}_{org} + HCr_2O^{-}_{7\ aq} \overset{K_{ex}}{\rightleftharpoons} (LH^{+},\ HCr_2O^{-}_{7})_{org} \quad (4)$$

According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} values using Eq. 3. Calculations of these constant values lead to log $K_{ex} = 3.24 \pm 0.2$ for **4** and log $K_{ex} = 3.49 \pm 0.2$ for **5**.

Conclusion

In conclusion, the synthesis and ion extraction abilities of *p-tert*-butylcalix[4]arenes based on *β*-ketoimine receptors (**4** and **5**) were studied. The spectroscopic data indicated

Scheme 2 Schematic illustration of proton-switchable extractant (4 and 5)



4 R: CH_3
5 R: Cl

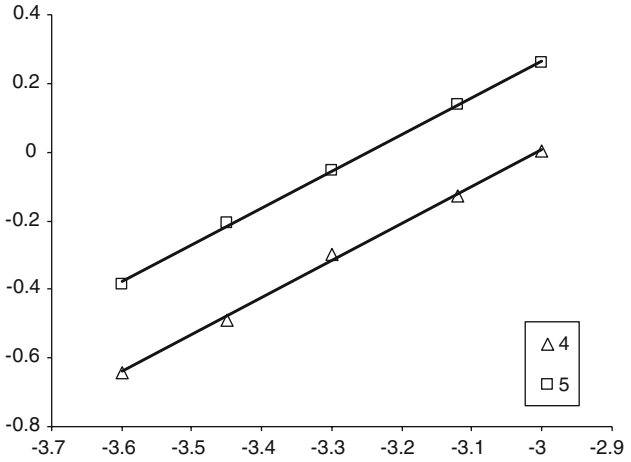


Fig. 2 Log *D* versus log[*L*] for the extraction of dichromate anions by the ligands 4 and 5 from an aqueous phase into dichloromethane at 25°C

that the new compounds are in the cone conformation. The dichromate anion studies showed that compounds **4** and **5** were effective receptors for $HCr_2O_7^-$ anion at low pH. The variety of hydrogen bonding sites that occur in these calix[4]arene derivatives may be of considerable importance for the future design of novel calix[4]arene-based receptors, carriers, or supramolecular structures. The calixarene based *β*-ketoimine receptors could be proved to find remarkable applications in the design of chemical sensors, in anion-binding processes, especially phase-transfer catalyses and solid-state sensors (ISFETs).

Experimental

General

All of the reagents used in this study were obtained from Merck or Fluka and used without further purification. Acetonitrile was dried from calcium hydride and stored under N_2 over molecular sieves (4 A°). CH_2Cl_2 was distilled from $CaCl_2$·MeOH over Mg and stored over molecular sieves. Anions were used as their sodium salts. Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck). Generally solvents were dried by storing them over molecular sieves (Aldrich; 4 A°, 8–12 mesh). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Column chromatographic separations were performed on Merck Silica gel-60 (230–400 mesh). The alkali metal picrates were prepared as described elsewhere [35]. Melting points were determined on a Gallenkamp apparatus. ^{1}H NMR spectra were obtained using a Varian 400 MHz spectrometer operating at 400 MHz. IR spectra were recorded on a Perkin–Elmer 1605 FTIR spectrometer as KBr pellets. UV–visible spectra were obtained on Jenway 6105 and Shimadzu 160 A UV–visible recording spectrophotometers. Elemental analyses were performed using a Leco CHNS-932 analyzer. An Orion 410A + pH meter was used for the pH measurements.

Synthesis

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (**1**) and 5,11,17,23-tetra-*tert*-butyl-25,27-di-(cyanomethoxy)-26,28-dihydroxycalix[4]arene (**2**) compounds were synthesized according to literature [27, 28]. The reduction of (**2**) to the corresponding amine compound 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(aminoethoxy)-26,28-dihydroxycalix[4]arene (**3**) was done according to literature procedure [29] and 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[(*β*-ketoimine)-ethoxy]-26,28-dihydroxycalix[4]arenes (**4**) and (**5**) were synthesized according to literature [25, 26]. All of the reactions were monitored with thin layer chromatography.

5,11,17,23-tetra-*tert*-butyl-25,27-bis-3-methyl-[(*β*-ketoimine)-ethoxy]-26,28-dihydroxycalix[4]arenes

About 2 mmol (1.30 g) of **3** in an ethanol/dichloromethane mixture (3:1) and molecular sieves are stirred for 30 minutes. To the mixture an excess of 3-methyl-2,4-pentanedione is then added gradually and heated under reflux during 36 h under nitrogen. The mixture is then filtered off and excess of solvent was evaporated under reduced pressure. The solid residue was purified by column chromatography on silica gel (EtOAc/n-hexane; 8:2) and recrystallized in CH_2Cl_2/MeOH to give **4** (1.0 g, 80%, m.p. 180–182°C with decomposition). ^{1}H NMR ($CDCl_3$): δ 0.88 (s, 18H, Bu^t), 1.29 (s, 18H, Bu^t), 1.94 (s, 6H), 2.12 (s, 6H), 2.27 (s, 6H), 3.28 (d, $J = 13.6$, 4H), 3.80 (q, 4H, $J = 6.7$), 4.0 (t, 4H), 4.20 (d, 4H, $J = 13.0$), 5.03 (s, 2H), 6.77 (s, 4H), 7.06 (s, 4H), 10.96 (t, 2H, $J = 6.8$); IR (ν) 3365 (NH,OH), 2900, 2875 (C–H), 1620 (CN), 1560, 1515, 1485 (C = C). Anal. Calc.: $C_{60}H_{82}N_2O_6$. C, 77.78; H, 8.84; N, 3.05%. Found: C, 77.69; H, 8.77; N, 3.03%.

5,11,17,23-tetra-*tert*-butyl-25,27-bis-3-chloro-[(*β*-ketoimine)-ethoxy]-26, 28-dihydroxycalix[4]arenes

About 2.5 mmol (1.70 g) of **3** in an ethanol/dichloromethane mixture (3:1) and molecular sieves are stirred for 30 min. To the mixture an excess of 3-chloro-2,4-pentanedione is then added gradually and heated under reflux during 36 h under nitrogen. The mixture is then filtered off

and excess of solvent was evaporated under reduced pressure. The solid residue was purified by column chromatography on silica gel (EtOAc/n-hexane; 8:2) and recrystallized in CH_2Cl_2/MeOH to give **5** (1.84 g, 76%, m.p. 205–209°C with decomposition). ^{1}H NMR ($CDCl_3$): δ 0.88 (s, 18H, Bu^t), 1.32 (s, 18H, Bu^t), 1.90 (s, 6H), 2.15 (s, 6H), 3.24 (d, $J = 13.6$, 4H), 3.84 (q, 4H, $J = 6.7$), 4.11 (t, 4H), 4.21 (d, 4H, $J = 13.0$), 5.01 (s, 2H), 6.72 (s, 4H), 7.02 (s, 4H), 11.10 (t, 2H, $J = 6.8$). IR (ν, cm^{-1}) 3380 (NH,OH), 2930, 2911 (C–H), 1615 (CN), 1563, 1510, 1495 (C = C). Anal. Calc.: $C_{58}H_{76}N_2O_6Cl_2$. C, 71.95; H, 7.85; N, 2.94%. Found: C, 71.69; H, 7.87; N, 2.90%.

Liquid–liquid extraction studies

The dichromate anion extraction experiments of calix[4]-arene β-ketoimin derivatives **4** and **5** were studied by liquid–liquid extraction experiments following Pedersen's procedure [36]. Into a vial was pipetted an aqueous solution (10 mL) containing the following: sodium dichromate at a concentration of 1×10^{-4} M, a few drops of 0.01 M KOH/HCl solution in order to obtain the desired pH at equilibrium and 10 mL of 1×10^{-3} M calixarene ligand in CH_2Cl_2. The mixture was 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 dichromate ion remaining in the aqueous phase was then determined spectrophotometrically as described previously [35, 37]. Blank experiments showed that no dichromate extraction occurred in the absence of calix[4]arene. The percent extraction (E%) was calculated from the absorbance A of the aqueous phase measured at 346 nm (for pH 1.5–4.5) using the following expression:

$$\text{Extraction } \% = (A_0 - A/\ A_0) \times 100$$

where A_0 and A are the initial and final concentrations of the dichromate ion before and after the extraction, respectively.

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