

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymer Supported Calix[4]arene Schiff Bases: A Novel Chelating Resin for Hg²⁺ and Dichromate Anions

Aysegül Karaküçük^a; Erdal Kocabas^a; Abdulkadir Sirit^a; Shahabuddin Memon^b; Mustafa Yilmaz^a; D. Max Roundhill^b

^a Department of Chemistry, Selçuk University, Konya, Turkey ^b Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas

To cite this Article Karaküçük, Aysegül , Kocabas, Erdal , Sirit, Abdulkadir , Memon, Shahabuddin , Yilmaz, Mustafa and Roundhill, D. Max(2005) 'Polymer Supported Calix[4]arene Schiff Bases: A Novel Chelating Resin for Hg²⁺ and Dichromate Anions', *Journal of Macromolecular Science, Part A*, 42: 6, 691 – 704

To link to this Article: DOI: 10.1081/MA-200058629

URL: <http://dx.doi.org/10.1081/MA-200058629>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polymer Supported Calix[4]arene Schiff Bases: A Novel Chelating Resin for Hg²⁺ and Dichromate Anions

AYSEGÜL KARAKÜÇÜK,¹ ERDAL KOCABAS,¹
ABDULKADIR SIRIT,¹ SHAHABUDDIN MEMON,²
MUSTAFA YILMAZ,¹ AND D. MAX ROUNDHILL²

¹Department of Chemistry, Selçuk University, Konya, Turkey

²Department of Chemistry and Biochemistry, Texas Tech University,
Lubbock, Texas

This article describes the synthesis and characterization of two new calix[4]arene Schiff bases and their polymeric resins. The extraction properties of these “proton switchable extractants” with alkali, transition, post transition metal cations and for dichromate anions are reported. The two new calix[4]arene based Schiff bases (5 and 6) have been synthesized from 5,17-diformyl-25,27-dipropoxy-26,28-dihydroxy-calix[4]arene (4) by treatment with 3-amino-methylpyridine and 1,8-diaminooctane in two separate reaction flasks following the same procedure. Compounds 5 and 6 have been appended to a polymeric resin by treatment with Merrifield resin through a nucleophilic substitution reaction. The receptor compounds (3 and 5–8) do not extract alkali metal cations, but show some selectivity toward transition metal cations, and a particularly high selectivity to Hg²⁺ and Pb²⁺. The protonated forms of all of the calixarene-based receptors are good extractants for transferring Cr₂O₇²⁻/HCr₂O₇⁻ anions from an aqueous into a dichloromethane layer.

Keywords calix[4]arene, Merrifield resin, Schiff base, proton-switchable, dichromate anions, solvent extraction

Introduction

Calixarenes are macrocyclic molecules that possess a unique three-dimensional structure with unique shaping and almost unlimited derivatization possibilities (1, 2). The easy accessibility and the selective functionalizations at the phenolic hydroxy groups (lower rim) and at the para positions of the phenol rings (upper rim) of calix[4]arenes have made this class of compounds increasingly attractive for chemists involved in host-guest and supramolecular chemistry (3). The majority of these modified calixarenes have a cavity suitable for the reception of different ionic and neutral species (4–9). The complexation properties of these molecules appear to be highly dependent upon the size

Received and Accepted November 2004

Address correspondence to Mustafa Yilmaz, Department of Chemistry, Selçuk University, 42031 Konya, Turkey. E-mail: myilmaz@selcuk.edu.tr

of the cavity, the nature and number of donor atoms, and on the conformation of the calix[4]arene moiety (10–12).

Anion recognition and sensing is an increasingly important research topic in supramolecular chemistry due to the involvement of various anions in biological and environmental situations. Chemists employ either electrostatic or hydrogen bonding interactions as binding devices for constructing anion receptors (13). The simultaneous binding of cationic and anionic guest species by ditopic receptors is a rapidly developing new field for ion pair recognition (14–16).

The importance of favorable amine, amide or protonated imine hydrogen bonding interactions for anion binding has recently been exploited in the design of calix[4]arene based anion receptors (17, 18) Tuntulani et al. (19) have synthesized tripodal azacrown ether calix[4]arenes containing simultaneous cation and anion binding sites, and have found that the binding ability toward Br^- is enhanced in the presence of K^+ . Rojsajjakul et al. (20) have synthesized polyaza crown ether derivatives of calix[4]arene and investigated their role as anion receptors. Beer and coworkers (21–23) have synthesized a number of receptors that can undergo selective ion pair recognition.

Chromate and dichromate anions are important because of their high toxicity and their presence in soils and waters (24–28). Chromium (VI) is a carcinogen in humans and animals, with chromates and dichromates being both mutagenic and genotoxic. Chromium (VI) is a widely used industrial chemical, and is generally considered to pose the greatest human health risk because it is more toxic, more soluble, and more mobile than is chromium (III). Chromium (VI) requires intracellular reduction for activation and this *in vivo* reduction can produce several reactive intermediates such as chromium (V) and chromium (IV) that can damage DNA (25). In designing complexants for these particular guest anions, a number of structural features can be incorporated into the host molecule that may be important in achieving selective binding. For a molecule to be effective as a host, it is necessary that its structural features are compatible with those of the guest anion. The chromate and dichromate (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$) ions are dianions with oxide functionalities at their periphery (29, 30). Consequently, since the periphery of the anions have oxide moieties, these are potential sites for hydrogen bonding to the host molecule. Roundhill et al. (31–33) have showed that the lower rim alkylammonium substituted calix[4]arenes act as “proton switchable extractants” for chromate and dichromate anions.

For certain applications such as the separation of anions and cations from aqueous media, or the fabrication of devices, it is important for a calixarene derivative to be available in insoluble form. Thus, calixarenes need to be modified chemically to reduce their solubility characteristics by immobilization on polymeric supports. The preparation of such insoluble polymeric calixarenes is done either by covalently linking the calixarene to the polymeric framework, or by connecting two calixarene by some spacer or functionality to give to resin like substance (34, 35). Such calixarene based polymers have just begun to receive attention since these new polymers can be processed into materials suitable for chemical sensor devices such as ion selective electrodes and filtration/extraction membranes (36–39).

In recent years, we have reported bifunctional receptors based on calix[4]arene for the recognition of alkali, transition and post transition metal cations and the chromate/dichromate anions (17, 30, 31, 40). Herein, we report the synthesis of new receptors containing calix[4]arene Schiff bases and their polymeric derivatives. The extraction properties of these products towards alkali metal, transition metal, and post transition metal cations, as well as toward the dichromate anion, have been studied.

Experimental

Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary. ^1H NMR spectra were recorded using a Varian 500 MHz spectrometer in CDCl_3 with TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV-Visible spectra were obtained on a Shimadzu 160 A UV-Visible recording spectrophotometer. Sodium determinations were made on a JENWAY PFP7 flame photometer. Elemental analysis data were performed on a Leco CHNS-932 analyzer. A Crison MicroPH 2002 digital pH meter was used for the pH measurements.

All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. Commercial grade solvents such as chloroform, methanol, acetone, ethylacetate and hexane were distilled, and then stored over 4 \AA molecular sieves. Acetonitrile and DMF were dried from calcium hydride and stored under N_2 over 4 \AA molecular sieves. Anions were used as their sodium salts. The drying agent employed was anhydrous MgSO_4 . Merrifield resin (0.8 mmol equivalent of Cl/g of resin) was purchased from Fluka. Analytical TLC was performed on pre-coated silica gel plates (SiO_2 , Merck PF254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

Synthesis

Compound **1–4** were synthesized according to previously published methods (41–44). Compounds **5–8** were synthesized as follows:

Calix[4]arene Schiff Base-I (5). To a solution of **4** (4.0 g, 7.08 mmol) in CHCl_3 (200 mL) was added a solution of 3-aminomethylpyridine (2.3 g, 21.24 mmol) in MeOH (50 mL) was refluxed for 24 h in the presence of MgSO_4 . The reaction mixture was allowed to cool to room temperature, and filtered. Evaporation of solvent and subsequent purification of mixture by column chromatography (Hexane/EtOAc 7 : 1 v/v), followed by recrystallization from $\text{CHCl}_3/\text{MeOH}$, afforded pure **5** (3.5 g) in 67% yield; m.p. 195–197°C (decomp.).

IR (KBr): 3320 cm^{-1} (OH) and 1638 cm^{-1} (C=N); ^1H NMR (CDCl_3) δ 1.33 (t, 6H, $J = 7.3\text{ Hz}$, $-\text{OCH}_2\text{CH}_2\text{CH}_3$), 2.18 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.47 (d, 4H, $J = 13.0\text{ Hz}$, ArCH_2Ar), 3.68 (s, 4H, $-\text{NCH}_2-\text{Py}$), 4.02 (t, 4H, $J = 6.2\text{ Hz}$, $-\text{OCH}_2\text{CH}_2\text{CH}_3$), 4.38 (d, 4H, $J = 13.0\text{ Hz}$, ArCH_2Ar), 6.83 (t, 2H, $J = 7.5\text{ Hz}$, ArH para), 6.96 (d, 4H, $J = 7.5\text{ Hz}$, ArH meta), 7.01–7.39 (m, 8H, Py-H), 7.62 (s, 4H, ArH meta), 7.86 (s, 2H, $-\text{N}=\text{CH}$), 8.32 (s, 2H, $-\text{OH}$). Anal. Calcd. for $\text{C}_{48}\text{H}_{48}\text{O}_4\text{N}_4$: C, 77.39%; H, 6.49%; N, 7.52%. Found: C, 77.16%; H, 6.86%; N, 7.38%.

Calix[4]arene Schiff Base-II (6). Compound **4** (2.0 g, 3.54 mmol) was dissolved in CHCl_3 (75 mL) and to this solution was added 1,8-diaminooctane (0.58 g, 4.04 mmol) in MeOH (15 mL). The reaction mixture was refluxed for 24 h, in the presence of MgSO_4 . After cooling to room temperature, the solvent was concentrated in vacuo to give the crude product. Purification by column chromatography (Hexane/EtOAc 7:1 v/v) gave **6**. Recrystallization of the solid from $\text{CHCl}_3/\text{MeOH}$ gave the pure compound **6** as yellow crystals (1.9 g) in 80% yield, m.p. 205–207°C.

IR (KBr): 3362 cm^{-1} (OH) and 1643 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ 1.26 (t, 6H, $J = 7.3$ Hz, $-\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.31 (m, 16H, $(\text{CH}_2)_8$), 2.12 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.38 (d, 4H, $J = 13.0$ Hz, ArCH_2Ar), 3.87 (t, 4H, $J = 6.2$ Hz $-\text{OCH}_2\text{CH}_2\text{CH}_3$), 4.24 (d, 4H, $J = 13.0$ Hz, ArCH_2Ar), 6.89 (t, 2H, $J = 7.5$ Hz, ArH para), 7.02 (d, 4H, $J = 7.5$ Hz, ArH meta), 7.58 (s, 4H, ArH meta), 7.73 (s, 2H, $-\text{N}=\text{CH}$), 8.44 (s, 2H, $-\text{OH}$). Anal. Calcd. for $\text{C}_{44}\text{H}_{52}\text{O}_4\text{N}_2$: C, 78.54%; H, 7.79%; N, 4.16%. Found: C, 78.32%; H, 8.03%; N, 4.04%.

General Procedure for Loading of Calix[4]arene Schiff Bases on Merrifield Resin (7 and 8). Sodium hydride (1.5 g, 62.5 mmol) was added to a three-neck flask under nitrogen flow, washed three times with 20 mL aliquots of petroleum ether. To this was added the solution of Merrifield resin (1.0 g) and 1.8 mmol of Schiff base derivative of calix[4]arene **5** or **6** in 50 mL dried DMF. The mixture was heated to 70°C and stirred for 2 days in the presence of sodium iodide (1.0 g). Excess solution was removed under vacuo and the polymeric beads were filtered, rinsed with water and 1 N HCl and then repeatedly washed with CHCl_3 and MeOH to ensure removal of any unreacted Schiff base. The beads were finally dried in a vacuum oven.

Polymer supported calix[4]arene Schiff bases (**7**) and (**8**) were prepared according to the procedure described above yielding 2.2 g and 2.1 g, respectively. Their nitrogen contents were about 0.16 mmol/g and 0.48 mmol/g, respectively. IR (KBr) spectrum of polymer **7**: 3336 cm^{-1} ($-\text{OH}$), 1638 cm^{-1} (C=N). IR (KBr) spectrum of polymer **8**: 3362 cm^{-1} ($-\text{OH}$), 1643 cm^{-1} (C=N).

Analytical Procedure

The picrate and/or dichromate extraction experiments of calix[4]arene Schiff bases (**5** and **6**) were studied by liquid-liquid extraction experiments following Pedersen's procedure (45). 10 mL of a 2.5×10^{-5} M aqueous picrate solution or a 1×10^{-4} M sodium dichromate solution (pH of the dichromate solution was maintained by 0.01 M KOH/HCl solution) and 10 mL of a 1×10^{-3} M solution of calixarene (**3/5/6**) in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, 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 picrate/dichromate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate/dichromate extraction occurred in the absence of calixarene. The percentage extraction ($E\%$) was calculated from the absorbance A of the aqueous phase measured at 372 nm (for picrate), and 346 nm (for dichromate at pH 1.5–4.5) using the following expression:

$$(E\%) = A_0 - A/A_0 \times 100 \quad (1)$$

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

Alkali picrates were prepared by the following method (52). A saturated solution of picric acid was prepared by dissolving the acid in hot (near boiling) water. Alkali carbonate (Na_2CO_3 , K_2CO_3 and Cs_2CO_3) was then added to the solution until no further carbon dioxide was evolved, and the solution pH tests as neutral. The color changed from yellow to orange and some precipitate started to form. As the solution was cooled gradually to 0°C, the alkali picrate forms a mass of crystals. The yield can

be maximized by evaporating the solvent to half of its original volume and then cooled it to 0°C, at which temperature additional crystals form. After washing with a small amount of cold water, the pure alkali picrates were dried under vacuum for 24 h and protected from moisture and light before use.

Lithium picrate was prepared by adding a saturated aqueous picric acid solution stepwise to LiOH until neutralization is reached. After evaporation of water, the residue was crystallized from ethyl acetate. The pure crystals were obtained by washing with a small amount of ethyl acetate, followed by drying under vacuum for 24 h and protection from moisture and light before use.

Ni²⁺, Cu²⁺, Co²⁺, and Cd²⁺ picrates were prepared from the respective metal carbonate (54). Lead picrate was prepared by dissolving picric acid in methanol and heated until no solid remained. This yielded a yellow solution to which an equal amount of lead monoxide was added. The methanol was heated further until boiling commenced and stirring was maintained. After the mixture began to boil lead picrate formed. Boiling was continued until the solution became a thick emulsion. It was then filtered and washed with methanol, the filtrate was then allowed to dry. Heating at 100°C for 2 h gave pure lead picrate. Hg²⁺ picrate was prepared *in situ* by dissolving excess of freshly prepared metal oxide or hydroxide, respectively, in a hot aqueous solution of picric acid. The mixture was stirred for 2–3 days and then filtered. After standing at room temperature for 24 h, the solution pH was measured, being in agreement with theoretical value.

Batchwise Adsorption of Selected Transition Metal Ions

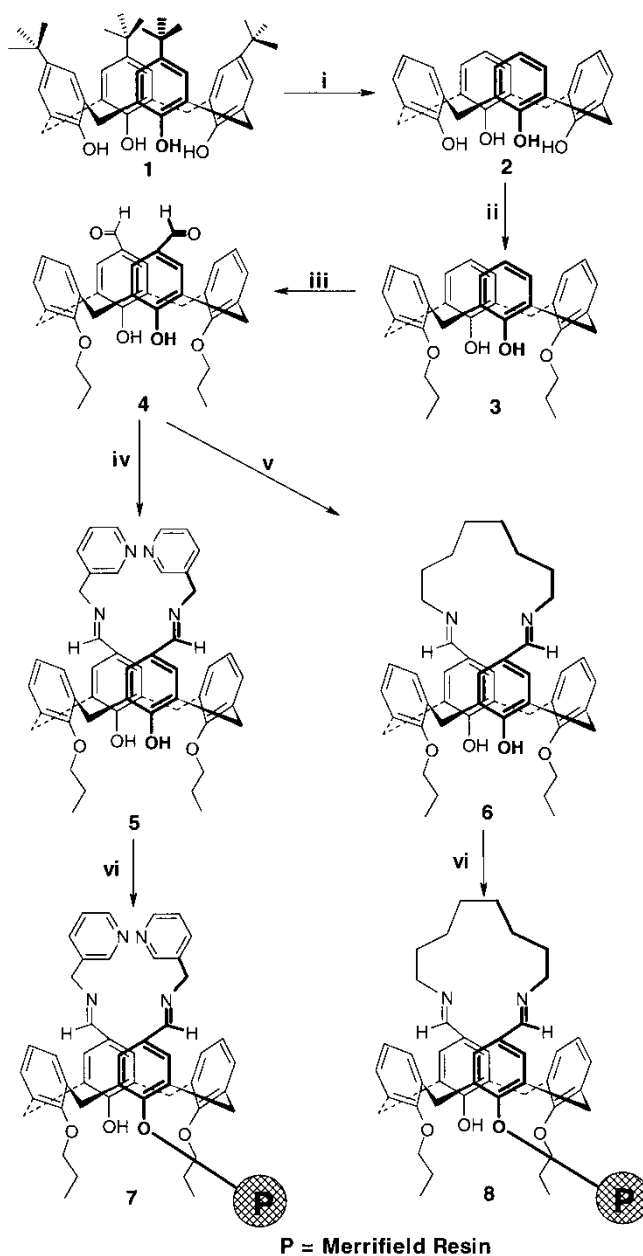
About 25 mg of the resin (**7** or **8**) was shaken with a 10 mL of aqueous solution containing 2.5×10^{-5} M metal picrate and/or dichromate in a 50 mL stoppered glass flask at 25°C for 1 h and filtered off. The concentration of metal picrate and/or dichromate ion remaining in aqueous phase after the adsorption was then determined spectrophotometrically. The adsorption percentage was calculated by the Equation (1).

Results and Discussion

Synthesis and Characterization

This work is mainly focused on the design of new calix[4]arene based ionophores which have an effective binding feature for a particular set of cations or anions, and could be useful for multiple applications such as environmental, laboratory and industrial process analysis. For the desired goal, *p-tert*-butylcalix[4]arene **1** was chosen as the starting material (41). The synthetic route is showed in Scheme 1. Compounds **1–4** have been prepared according to the previously published literature procedures (41–44), while reaction steps leading from **5** to **8** are described for the first time. Following the strategy outlined in Scheme 1, the compounds **5** and **6** have been obtained respectively from the compound **4** by treatment with 3-aminomethylpyridine or 1,8-diaminooctane in the presence of MgSO₄ in CHCl₃/MeOH under reflux. These compounds have been supported onto Merrifield resin (**7** and **8**) in the presence of NaH and NaI in dry DMF.

All of the new compounds have been characterized by a combination of IR, ¹H NMR and elemental analysis. From ¹H NMR data, **5** and **6** exhibit a singlet at δ 7.86 ppm and 7.73 ppm, respectively, which indicates the presence of HC=N. These compounds were confirmed to be present in the cone conformation from the ¹H NMR spectra (doublets



Scheme 1. (i) Phenol, AlCl_3 , toluene; (ii) *n*-PrBr, MeCN, K_2CO_3 , NaI; (iii) TiCl_4 , dichloromethyl methyl ether, CHCl_3 ; (iv) 3-methylpyridine, $\text{CHCl}_3/\text{MeOH}$; (v) 1,8-diamino octane, $\text{CHCl}_3/\text{MeOH}$; (vi) Merrifield resin, DMF, NaH, NaI.

at δ 3.47 ppm, 4.38 ppm $J = 13.0$ Hz and at δ 3.38 ppm, 4.24 ppm $J = 13.0$ Hz for ArCH_2Ar protons of **5** and **6**, respectively).

From the elemental analysis data the nitrogen contents of polymer supported calix[4]-arene Schiff bases (**7** and **8**) have been calculated to be about 0.16 mmol/g and

0.48 mmol/g, respectively, which shows that the calix[4]arene Schiff bases (**5** and **6**) are coupled to the Merrifield resin in good yield. This conclusion has also been confirmed by a strong C=N (1638, 1643 cm^{-1}) band in the FT-IR spectra of polymers **7** and **8**. Thus, polymer **7** contains *ca.* one calixarene unit to five styrene units, while polymer **8** contains *ca.* one calixarene unit to two styrene units in the polymeric backbone respectively. The results indicate that unreacted chloro-groups on the Merrifield resin could not be substituted by phenolic groups of calix[4]arene Schiff bases (**5** and **6**), possibly due to unfavorable steric interactions of the large macrocycle. The results are also consistent with ruling out the possibility of ethanolic NaOH replacing unreacted chloro groups in the resin (**50**).

Metal Cation Extraction

The present work is focused on discovering the favorable requirements for obtaining effective two-phase extractants. Solvent extraction experiments were performed to ascertain the effectiveness of compounds **3**, **5** and **6** in transferring alkali metal, transition metal and post transition metal cations such as Li^+ , Na^+ , K^+ , Cs^+ , Hg^{2+} , Pb^{2+} , Cu^{2+} , Co^{2+} , Cd^{2+} and Ni^{2+} from an aqueous phase into an organic phase. The results of the picrate extraction studies are summarized in Table 1 (Figure 1). These data have been obtained using a dichloromethane solution of the receptors **3**, **5** and **6** to extract metal picrates from aqueous solution. The equilibrium concentration of picrate in the aqueous phase has been determined spectrophotometrically.

From the data in Table 1, it is observed that neither alkali nor transition metal cations are significantly extracted by the 1,3-dialkyl substituted calix[4]arene **3**. Imine groups in **5** and **6** improves the extraction ability toward transition metal cations, especially for Hg^{2+} and Pb^{2+} . The increase in the extraction of metal ions with **5** and **6** is due to the presence of soft binding sites, which are provided by the imine groups. This is in agreement with our previous work (31, 46).

In order to observe the extraction properties of more than one ionophore unit bound together, polymeric resins **7** and **8** have been synthesized. The solid-liquid extraction experiments show that both resins (**7** and **8**) retain their inherent selective nature and exhibit good extraction ability for Hg^{+2} (Table 1, Figure 1).

Table 1
Extraction of metal picrates with ligands^a

Ligand	Picrate salt extracted (%)									
	Li^+	Na^+	K^+	Cs^+	Co^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Hg^{2+}
3	<0.1	2.5	<0.1	<0.1	<0.1	<0.1	<0.1	2.8	5.9	6.0
5	<0.1	<0.1	<0.1	6.0	4.2	4.9	5.8	3.5	22.5	57.1
6	<0.1	<0.1	<0.1	6.8	4.7	4.4	6.6	3.8	23.7	58.9
7^b	3.3	<0.1	<0.1	7.5	7.1	8.2	9.0	7.0	19.6	52.7
8^b	5.3	<0.1	<0.1	8.3	7.4	8.5	9.1	7.1	16.3	49.9

^aAqueous phase, [metal nitrate] = 1×10^{-2} M; [picric acid] = 2.5×10^{-5} M; organic phase, dichloromethane, [ligand] = 1×10^{-3} M at 25°C, for 1 h.

^bSolid-liquid batchwise adsorption extraction experiments.

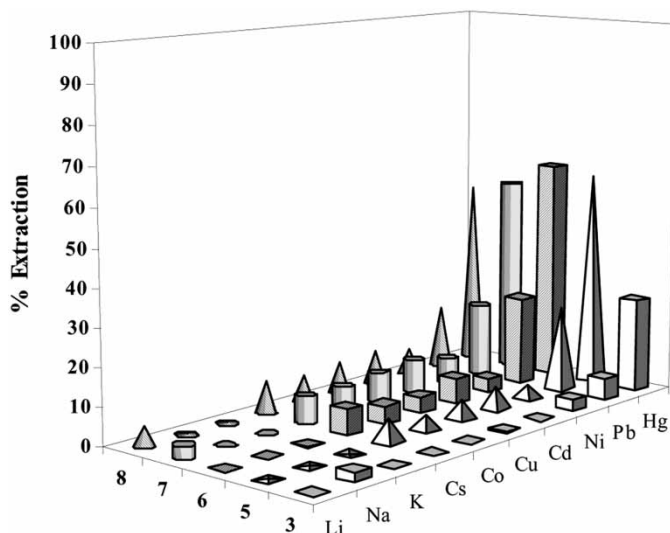


Figure 1. Extraction percentage of alkali and transition metal cations with **3**, **5**, **6**, **7** and **8**.

Dichromate Anion Extraction

In recent years a number of modified calixarenes have been synthesized that can be used as host for various anions (19, 20, 47, 49, 51). This has occurred because the periphery of a chemically modified calixarene can be made structurally compatible with these ions. Therefore, our goal is the synthesis of extractants based on a calix[4]arene framework that are especially effective for dichromate anions. The dichromate ($\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$) ions are dianions where the periphery of the anion have oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. A preliminary evaluation of the extraction efficiencies of **5** and **6** have been carried out by solvent extraction of $\text{Na}_2\text{Cr}_2\text{O}_7$ from aqueous phase into dichloromethane at different pH values. The extraction results are presented in Table 2. From the extraction data it is clear that the extractant **5** is more effective for the extraction of dichromate anions at low pH (1.5–2.5) because **5** contains a proton-switchable pyridinium and imine binding site appropriate for aggregation of anions at low pH. Observations show that the extraction ratio decreases as the pH increases, showing that the protonated form of **5** is an effective host for the dichromate anions (Figure 2, Table 2). From the extraction data given in Table 2, it is apparently clear that **3** has not extracted $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$ ions significantly. However the conversion of **3** into a cyclic Schiff base derivative **6** increases the anion extraction ability of this compound to a remarkable extent. This pronounced increase may be due to more rigid structural features, and the protonation of imine groups of **6**, both of which may assist in transferring anions as compared to **3**. Therefore, it can be demonstrated that because of the proton transfer to the nitrogen atom of the pyridine/imine unit in **5** and **6**, an ion pair complex is formed in the two phase extraction system (Scheme 2). Both Schiff base derivatives of calix[4]arene show enhanced ion pair extraction of the sodium salt of chromium (VI) even at low pH. This observation can be explained by the fact that the hydrophilic nature of the OH groups may affect the extraction ability of these compounds due to their interaction at the water-dichloromethane interface which may

Table 2
Percentage extraction of dichromate by extractants
5 and **6** at different pH values^a

Compound	Dichromate anion extracted (%), pH			
	1.5	2.5	3.5	4.5
3	9.2	12.8	11.3	10.8
5	57.3	41.6	22.6	2.2
6	52.7	31.8	11.8	<0.1
7^b	23.5	16.2	<0.1	<0.1
8^b	28.2	18.1	<0.1	<0.1

^aAqueous phase, [metal dichromate] = 1×10^{-4} M; organic phase, dichloromethane, [ligand] = 1×10^{-3} M at 25°C, for 1 h. The percentage extraction is given by [initial aqueous anion] - [final aqueous anion]/[initial aqueous anion] \times 100.

^bSolid-liquid batchwise adsorption extraction experiments.

provide a proton exchange process in transferring Na^+ ions. Upon addition of NaOH to the aqueous layer, the deprotonated calixarene **5** and **6** in the dichloromethane layer is no longer an effective host molecule for $\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$, and the dianion migrates back into the aqueous layer in a reversible process (Scheme 2).

This feature is very important if it is desirable to recover the metal in pure form and for the extractant to be available for reuse (33). The solid-liquid batchwise adsorption extraction experiments (48, 52) of the polymer supported calix[4]arene Schiff bases **7** and **8** have been performed in aqueous solutions of $\text{Cr}_2\text{O}_7^{2-}$ at various pH values. From the data in Table 2, it is clear that there is a significant decrease in the extraction ability of the polymers **7** and **8** over the monomers **5** and **6**. Nevertheless they show good affinity toward $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$ at low pH (Table 2).

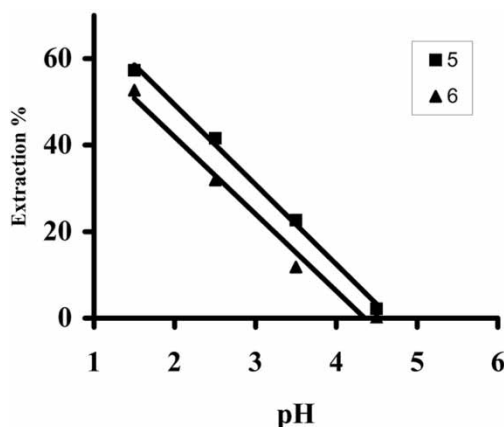
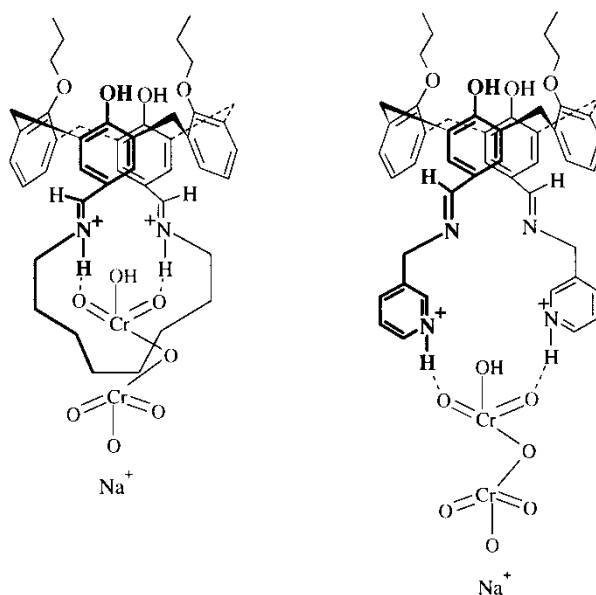
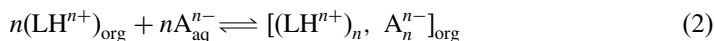


Figure 2. Plots of extraction (E %) vs. pH following the two phase solvent extraction of dichromate with compounds **5** and **6**.



Scheme 2. The proposed interactions of compound **5** and **6** with Na^+ and HCr_2O_7^- ions.

All data have been analyzed using the classical slope analysis method. Assuming that the extraction of an anion A^{n-} by the receptor LH^{n+} is according to following equilibrium:



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

$$K_{\text{ex}} = \frac{[(\text{LH}^{n+})_n, \text{A}_n^{n-}]_{\text{org}}}{[\text{A}^{n-}]_{\text{aq}}^n [\text{LH}^{n+}]_{\text{org}}^n} \quad (3)$$

Equation (3) can be re-written as:

$$\log D_A = \log K_{\text{ex}} + n \log [\text{LH}^{n+}]_{\text{org}} \quad (4)$$

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

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

Consequently a plot of the $\log D_A$ vs. $\log [\text{L}]$ may lead to a straight line with a slope that allows for the determination of the stoichiometry of the extracted species, where $[\text{L}]$ is defined as the analytical concentration of the ligand in the organic phase. Figure 3 represents the extraction into dichloromethane at different concentrations of **5** and **6** with dichromate respectively. A linear relationship between $\log D_A$ vs. $\log [\text{L}]$ is observed with a slope of line for the dichromate anion by **5** and **6** that is approximately equal to 1 at pH 1.5, suggesting that **5** and **6** form a 1:1 complex with dichromate anion. This is attributed to the presence of following equilibrium:



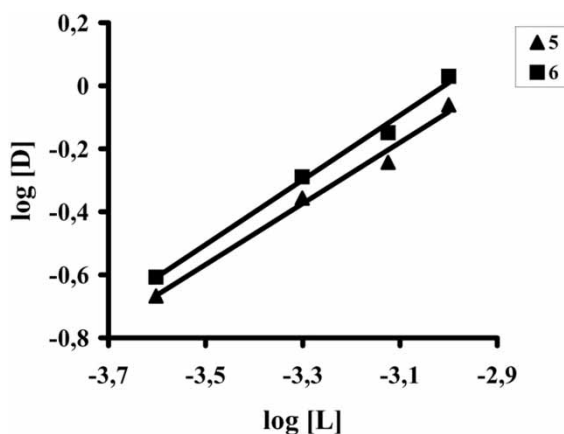
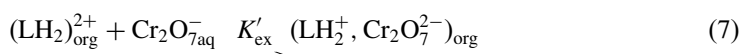
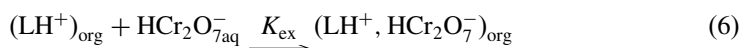


Figure 3. Log D vs. log [L] for the extraction of dichromate by the ligand **5** and **6** from an aqueous phase into dichloromethane at 25°C.

At high acidic conditions $\text{Na}_2\text{Cr}_2\text{O}_7$ is converted into the $\text{H}_2\text{Cr}_2\text{O}_7$ form, and after the ionization in aqueous solution it exists in the $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$ form. This allows us to consider this simultaneous extraction of 1:1 complexes according to the following equilibria:



According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} and K'_{ex} values using Equation (4.) Calculations of these constant values lead to $\log K_{\text{ex}} = \log K'_{\text{ex}} = 3,03 \pm 0,2$ for **5** and $\log K_{\text{ex}} = \log K'_{\text{ex}} = 2,83 \pm 0,2$ for **6**.

Conclusions

This work reported here allows further conclusions to be made about the description of simple calixarene host-guest compounds. Two new calix[4]arene Schiff base derivatives **5** and **6** in the cone conformation have been synthesized from 5,17-diformyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene **4** by treatment with 3-aminomethylpyridine or 1,8-diaminooctane respectively. These Schiff base derivatives of calix[4]arene have been supported to a Merrifield resin to obtain multiple calix[4]arene units. The newly synthesized compounds **5** and **6** and their polymeric derivatives **7** and **8** show good affinity and selectivity toward Hg^{2+} . Extraction studies of all of the new calix[4]arene derivatives with alkali/transition metal cations and their systematic complexation studies are presented here for $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$ anions at different pH values. This work confirms the good selectivity of **5** and **6** toward Hg^{2+} and Pb^{2+} cations from an aqueous solution as compared to the unsubstituted calix[4]arene **3**. Compounds **5** and **6** are good extractants for $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$ anions, but their polymeric derivatives **7** and **8** have poor affinity for $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$ at high pH in the solid-liquid extraction system. We have also shown that the calixarenes substituted at the upper rim with

imine groups and/or pyridine containing ionophoric moieties show proton-switchable extraction. This hydrogen bonding motifs that occur in these calix[4]arene Schiff base derivatives may be of considerable importance for the future design of novel calix[4]arene based receptors, carriers, or supramolecular structures.

Acknowledgements

We thank the Robert A Welch Foundation (Grant Number D-1408), the US National Science Foundation (Grant Number INT-0111170), and the Scientific and Technical Research Council of Turkey (TUBITAK-Grant Number U/9-101T002) for financial support of this work.

References

1. Gutsche, C.D. (1998) *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge.
2. Vicens, J. and Böhmer, V. (1991) *Calixarenes: A Versatile Class of Macrocyclic Compounds Topics in Inclusion Science*; Kluwer Academic: Dordrecht.
3. Asfari, Z., Böhmer, V., Harrowfield, J.McB., and Vicens, J. (2001) *Calixarenes 2001*; Kluwer Academic Publishers: Dordrecht.
4. Beer, P.D., Drew, M.G.B., Heseck, D., and Nam, K.C. (1997) A New Carboxylate Anion Selective Cobaltocenium Calix[4]arene Receptor. *Chem. Commun.*, 107–108.
5. Scheerder, J., Fochi, M., Engbersen, J.F.L., and Reinhoudt, D.N. (1994) Urea-derivatized p-tert-butylcalix[4]arenes: Neutral Ligands for Selective Anion Complexation. *J. Org. Chem.*, 59: 7815–7820.
6. Gutsche, C.D. and See, K.A. (1992) Calixarenes. 27. Synthesis, Characterization, and Complexation Studies of Double-Cavity Calix[4]arenes. *J. Org. Chem.*, 57: 4527–4539.
7. Van Loon, J.D., Janssen, R.G., Verboom, W.D., and Reinhoudt, D.N. (1992) Hydrogen Bonded Calix[4]arene Aggregates. *Tetrahedron Lett.*, 33: 5125–5128.
8. Morzherin, Y., Rudkevich, D.M., Verboom, W., and Reinhoudt, D.N. (1993) Chlorosulfonylated Calix[4]arenes: Precursors for Neutral Anion Receptors with a Selectivity for Hydrogen Sulfate. *J. Org. Chem.*, 58: 7602–7605.
9. Beer, P.D., Chen, Z., Goulden, A.J., Graydon, A., Stokes, S.E., and Wear, T. (1993) Selective Electrochemical Recognition of the Dihydrogenphosphate Anion in the Presence of Hydrogen-sulphate and Chloride Ions by New Neutral Ferrocene Anion Receptors. *J. Chem. Soc.: Chem. Commun.*, 1834–1841.
10. Arnaud-Neu, F., Barrett, G., Harris, S.J., Owens, M., McKerverey, M.A., Schwing-Weill, M.J., and Schwinte, R. (1993) Cation Complexation by Chemically Modified Calixarenes. 5. Protonation Constants for Calixarene Carboxylates and Stability Constants of their Alkali and Alkaline-earth Complexes. *Inorg. Chem.*, 32: 2644–2650.
11. Ghidini, E., Ugozzoli, F., Ungaro, R., Harkema, S., Abu El-Fadl, A., and Reinhoudt, D.N. (1990) Complexation of Alkali Metal Cations by Conformationally Rigid, Stereoisomeric calix[4]arene Crown Ethers: A Quantitative Evaluation of Preorganization. *J. Am. Chem. Soc.*, 112: 6979–6985.
12. Talanova, G.G., Hwang, H.-S., Talanov, V.S., and Bartsch, R.A. (1998) Calix[4]arenes with Hard Donor Groups as Efficient Soft Cation Extractants. Remarkable Extraction Selectivity of Calix[4]arene N-(X)sulfonylcarboxamides for Hg^{II}. *Chem. Commun.*, 1329–1330.
13. Steed, J.W. and Atwood, J.L. (2000) *Supramolecular Chemistry*; John Wiley & Sons: New York.
14. Scheerder, J., Van Duynhoven, J.P.M., Engbersen, J.F.F., and Reinhoudt, D.N. (1996) Solubilization of NaX Salts in Chloroform by Bifunctional Receptors. *Angew. Chem. Int. Ed. Engl.*, 35: 1090–1093.

15. Pelizzi, N., Casanati, A., Friggeri, A., and Ungaro, R. (1998) Synthesis and Properties of New Calixarene-Based Ditopic Receptors for the Simultaneous Complexation of Cations and Carboxylate Anions. *J. Chem. Soc.: Perkin Trans.*, 2: 1307–1312.
16. Beer, P.D. and Cooper, J.B. (1998) Alkali Metal Cation Cooperative Iodide Anion Recognition by New Heteroditopic Bis(calix[4]arene) Rhenium(I) Bipyridyl Receptor Molecules. *Chem. Commun.*, 129–130.
17. Memon, S. and Yilmaz, M. (2001) A Complimentary Study of Calixarene Based Bifunctional Receptors for Alkali or Transition Metal Cations and $\text{Cr}_2\text{O}_7^{2-}$ Anions. *J. Mol. Struct.*, 595: 101–109.
18. Sessler, J.L., Andrievsky, A., Gale, P.A., and Lynch, V. (1996) Anion Binding: Self-assembly of Polypyrolic Macrocycles. *Angew. Chem. Int. Ed. Eng.*, 3: 2782–2785.
19. Tuntulani, T., Poompradub, S., Thavornnyutikarn, P., Jaiboon, N., Ruangpornvisuti, V., Chaichit, N., Asfari, Z., and Vicens, J. (2001) Aza Crown Ether Calix[4]arenes Containing Cation and Anion Binding Sites: Effects of Metal Ions Towards Anion Binding Ability. *Tetrahedron Lett.*, 42: 5541–5544.
20. Rojsajakul, T., Veragong, S., Tumcharearn, G., Seangprasertkij, R., and Tuntulani, T. (1997) Synthesis and Characterization of Polyaza Crown Ether Derivatives of Calix[4]arene and their Role as Anion Receptors. *Tetrahedron*, 53: 4669–4680.
21. Redman, J.E., Beer, P.D., Dent, S.W., and Drew, M.G.B. (1998) Cooperative Binding of Potassium Cation and Chloride Anion by Novel Rhenium(I) Bipyridyl Amide Crown Ether Receptors. *Chem Commun.*, 231–232.
22. Beer, P.D., Hopkins, P.K., and McKinney, J.D. (1999) Cooperative Halide, Perrhenate Anion-Sodium Cation Binding and Perchnetate Extraction and Transport by a Novel Tripodal Tris(amido benzo-15-crown-5) Ligand. *Chem. Commun.*, 1253–1254.
23. Cooper, J.B., Drew, M.G.B., and Beer, P.D. (2000) Alkali Metal Cation Cooperative Anion Recognition by Heteroditopic Bis(calix[4]arene) Rhenium(I) Bipyridyl and Ferrocene Receptor Molecules. *J. Chem. Soc.: Dalton Trans.*, 2721–2724.
24. Bartsch, R.A. and Way, J.D. (1996) *Chemical Separations with Liquid Membranes*; American Chemical Society: Washington DCACS Symposium Series No. 462.
25. Stearns, D.M., Kennedy, L.J., Courtney, K.D., Giangrande, P.H., Phieffer, L.S., and Wetterhahn, K.E. (1995) Reduction of Chromium(VI) by Ascorbate Leads to Chromium-DNA Binding and DNA Strand Breaks *in vitro*. *Biochemistry*, 34: 910–919.
26. Wittbrodt, P.R. and Palmer, C.D. (1995) Reduction of Cr(VI) in the Presence of Excess Soil Fulvic Acid. *Environ. Sci. Technol.*, 29: 255–263.
27. Burrows, D. (1983) *Chromium: Metabolism and Toxicity*; CRC Press: Boca Raton, FL.
28. De Flora, S. and Wetterhahn, K.E. (1989) Mechanism of Chromium Metabolism and Genotoxicity. *Life Chem. Rep.*, 7: 169–244.
29. Roundhill, D.M. and Koch, H.F. (2002) Methods and Techniques for the Selective Extraction and Recovery of Oxoanions. *Chem. Soc. Rev.*, 31: 60–67.
30. Yilmaz, A., Memon, S., and Yilmaz, M. (2002) Synthesis and Study of Allosteric Effects on Extraction Behavior of Novel Calixarene-Based Dichromate Anion Receptors. *Tetrahedron*, 58: 7735–7740.
31. Tabakci, M., Memon, S., Yilmaz, M., and Roundhill, D.M. (2003) Synthesis and Extraction Studies of a Versatile Calix[4]arene-Based “Proton-Switchable Extractant” for Toxic Metals and Dichromate Anions. *J. Inc. Phenom. Mac. Chem.*, 45: 265–270.
32. Falana, O.M., Koch, H.F., Roundhill, D.M., Lumetta, C.J., and Hay, B.P. (1998) Synthesis and Extraction Studies of 1,2- and 1,3-Disubstituted Butylcalix[4]arene Amides with Oxyions, Geometric and Conformational Effects. *J. Chem. Soc.: Chem. Commun.*, 503–504.
33. Georgiev, M., Wolf, N., and Roundhill, D.M. (1997) Lower Rim Alkylammonium-Substituted Calix[4]arenes as “Proton-Switchable” Extractants for Chromate and Dichromate Anions. *Polyhedron*, 16: 1581–1584.
34. Trivedi, U.V., Menon, S.K., and Agrawal, Y.K. (2002) Polymer Supported Calix[6]arene Hydroxamic Acid, A Novel Chelating Resin. *React. Funct. Polym.*, 50: 205–216.

35. Jain, V.K., Handa, A., Pandya, R., Shrivastav, P., and Agrawal, Y.K. (2002) Polymer Supported Calix[4]arene-semicarbazone Derivative for Separation and Preconcentration of La(III), Ce(III), Th(IV) and U(VI). *React. Funct. Polym.*, 51: 101–110.
36. Shinkai, S., Kawaguchi, H., and Manabe, O. (1998) Selective Adsorption of UO₂²⁺ to a Polymer Resin Immobilizing Calixarene-Based Uranophiles. *J. Pol. Sci.: Part C, Polymer Lett.*, 26: 391–396.
37. Zheng, Y.S. and Huang, Z.T. (1998) Synthesis of Oligomers of Calix[4]arene with Methylene Bridge at the Upper Rims. *Tetrahedron Lett.*, 39: 5811–5814.
38. Nishikubo, T., Kameyama, A., Tsutsui, K., and Iyo, M. (1999) Synthesis and Photochemical Reaction of Novel p-alkylcalix[n]arene Derivatives Containing Cationically Polymerizable Groups. *J. Polym. Sci. A: Polym. Chem.*, 37: 1805–1814.
39. Memon, S., Uysal, G., and Yilmaz, M. (2001) Syntheses and Binding Properties of Polymeric Calix[4]crown-4. *React. Funct. Polym.*, 47: 165–174.
40. Ediz, O., Tabakci, M., Memon, S., Yilmaz, M., and Roundhill, D.M. (2004) A Convenient Approach towards the Synthesis of a “Proton Switchable” Chromium(VI) Extractant Based on Calix[4]arene. *Supramol. Chem.*, 16: 199–204.
41. Gutsche, C.D., Iqbal, M., and Stewart, D. (1986) Calixarenes. 19. Syntheses Procedures for p-tert-butylcalix[4]arene. *J. Org. Chem.*, 51: 742–745.
42. Gutsche, C.D., Levine, J.A., and Sujeeth, P.K. (1985) Calixarenes. 17. Functionalized Calixarenes: the Claisen Rearrangement Route. *J. Org. Chem.*, 50: 5802–5806.
43. Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Egberink, R.J.M., De Song, F., and Reinhoudt, D.N. (1995) Synthesis, Complexation, and Membrane Transport Studies of 1,3-Alternate Calix[4]arene-crown-6 Conformers: A New Class of Cesium Selective Ionophores. *J. Am. Chem. Soc.*, 117: 2767–2777.
44. Arora, V., Chawla, H.M., and Santra, A. (2002) Synthesis of Selectively Formylated Calixarene Ethers. *Tetrahedron*, 58: 5591–5597.
45. Pedersen, C.J. (1968) Ionic Complexes of Macrocyclic Polyethers. *J. Fed. Proc. Fed. Am. Soc. Exp. Biol.*, 27: 1305–1309.
46. Memon, S. and Yilmaz, M. (2000) Synthesis and Complexation Studies of 1,3-dialkylated p-tert-butylcalix[4]arene Telomers. *React. Funct. Polym.*, 44: 227–233.
47. Nam, K.C., Kang, S.O., Jeong, H.S., and Jeon, S. (1999) Urea Derivative of Calix[4]diquinone: HSO₄⁻ Ion Selective Receptor. *Tetrahedron Lett.*, 4: 7343–7346.
48. Deligöz, H. and Yilmaz, M. (1995) Liquid-Liquid Extraction of Transition Metal Cations by Calixarenes-Based Cyclic Ligands. *Solvent Extr. Ion. Exch.*, 13: 19–26.
49. Inoue, K., Hýrakawa, H., Ishikowa, Yamaguchi, Y.T., Nagata, J., Ohto, K., and Yoshikuza, K. (1996) *Separation Sci. Tech.*, 31: 2273.
50. Alexandratos, D. and Natesan, S.S. (2000) Synthesis and Ion-Binding Affinities of Calix[4]-arenes Immobilized on Cross-Linked Polystyrene. *Macromolecules*, 34: 206–210.
51. Duhart, A., Dozol, J.F., Rouquette, H., and Deratani, A. (2001) Selective Removal of Cesium From Model Nuclear Waste Solutions Using A Solid Membrane Composed of an Unsymmetrical Calix[4]arenebis-crown-6 bonded to an Immobilized Polysiloxane Backbone. *J. Memb. Sci.*, 185: 145–155.
52. Tabakci, M., Memon, S., Yilmaz, M., and Roundhill, D.M. (2004) Synthesis and Evaluation of Extraction ability of Calix[4]-crown-6 Cone Conformer and its Oligomeric Analogue. *React. Funct. Polym.*, 58: 27–34.
53. Tabakci, M., Memon, S., Sap, B., Roundhill, D.M., and Yilmaz, M. (2004) A Calix[4]arene Derived Dibenzonitrile Receptor Modified at its “Lower Rim” by a Polymerizable Group. *J. Macromol. Sci. Part A: Pure and Appl. Chem.*, 4: 811–825.
54. Bartsch, R.A., Yang, I.W., Jeon, E.G., Walkowiak, W., and Charewicz, W.A. (1992) Selective Transport of Alkali Metal Cations in Solvent Extraction by Proton-Ionizable Dibenzocrown Ethers. *J. Coord. Chem.*, 27: 75–85.