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ScienceDirect
Tetrahedron 63 (2007) 5000–5005
Tetrahedron

Synthesis and dichromate anion extraction ability of *p-tert*-butylcalix[4]arene diamide derivatives with different binding sites

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Received 9 November 2006; revised 3 March 2007; accepted 22 March 2007
Available online 27 March 2007

Abstract—The article describes the synthesis and evaluation of the dichromate anion ($Cr_2O_7^{2-}$/$HCr_2O_7^-$) extraction properties of *p-tert*-butylcalix[4]arene diamide derivatives (**5**–**7**) containing different binding sites. Among these compounds, **6** and **7** have been synthesized via aminolysis in a toluene–methanol solvent system with 3-aminomethylpyridine and 3,6-dioxa-1,8-diamino octane, respectively. On the other hand, compound **5** has been synthesized via an acid chloride method due to its inefficiency under aminolysis. The extraction properties of these diamides toward dichromate anions are studied by liquid–liquid extraction. The results show that *p-tert*-butylcalix[4]arene diamide derivative **7** exhibited a much higher affinity toward dichromate anions than that of **6** due to its special structure, while **5** was an ineffective ligand for these anions.

1. Introduction

Toxic heavy metals like copper, mercury, chromium, lead, nickel, and cadmium can have a serious impact on the aqueous environment, as well as on animals and humans. Chromium and its compounds are widely used in the plating, leather tanning, dye, cement, and photography industries, producing large quantities of toxic pollutants.[1] Chromium can exist in several oxidation states, however, only the trivalent and hexavalent forms are environmentally important.[2] Chromium(III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid, and protein metabolism. Chromium(VI) can be toxic as it can diffuse as $Cr_2O_7^{2-}$ or $HCr_2O_7^-$ through cell membranes, and oxidize biological molecules.[3] The maximum permissible levels of Cr(VI) in potable and industrial wastewaters are 0.05 and 0.25 mg/L, respectively.[2] Due to its high solubility, Cr(VI) is very toxic to living organisms compared to Cr(III).[4] When Cr(VI) is ingested beyond the maximum concentration, it can cause health disorders, such as vomiting and haemorrhage.[5] Therefore, treatment of wastewater containing Cr(VI) prior to discharge is essential. Conventional techniques for removing metal ions from wastewater include chemical precipitation, membrane separation, reverse osmosis, evaporation, electrochemical treatment, and solvent extraction. Among them, solvent extraction is one of the most commonly used treatment methods, and employs a selective complexant especially for ions in aqueous solution. Although there are numerous examples of molecules that act as hosts and complexants for cations, relatively few molecules have been reported as hosts for anions.[6–9] Thus, the development of an efficient extractant for anions has received considerable attention in recent years.[10]

Calixarenes, cyclic oligomers of phenolic units linked through the *ortho* positions, are a fascinating class of macrocycle. Chemical modification from the upper or lower rim has made this class of synthetic ionophores as effective extractants for transferring anionic and cationic ions or neutral molecules from aqueous solution into an organic layer. The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms, and also upon the conformation of the calix[4]arene moiety.[11–14] Therefore, a variety of sophisticated anion complexing ligands containing a calix[4]arene backbone have been designed and synthesized for use as selective anion extractants.[15–18] These molecules are generally calix[4]arene derivatives bearing amine or amide functions, and are capable of interacting with anions by hydrogen bonds or cation–π interactions.[19] In recent years, we have reported calix[4]arene based receptors that effectively bind anions, which can be useful in multiple applications such as laboratory, clinical, environmental, and industrial process analyses.[20–23] In the literature, generally, although amine derivatives of calix[4]arene are known to be more effective extractants than its amide derivatives for anions, the preparation of their amide derivatives is also important since their stability is more than that of amine derivatives. Therefore, herein, we report the syntheses and dichromate anion

Keywords: *p-tert*-Butylcalix[4]arene; Diamide; Dichromate anions; Extraction.
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doi:10.1016/j.tet.2007.03.138

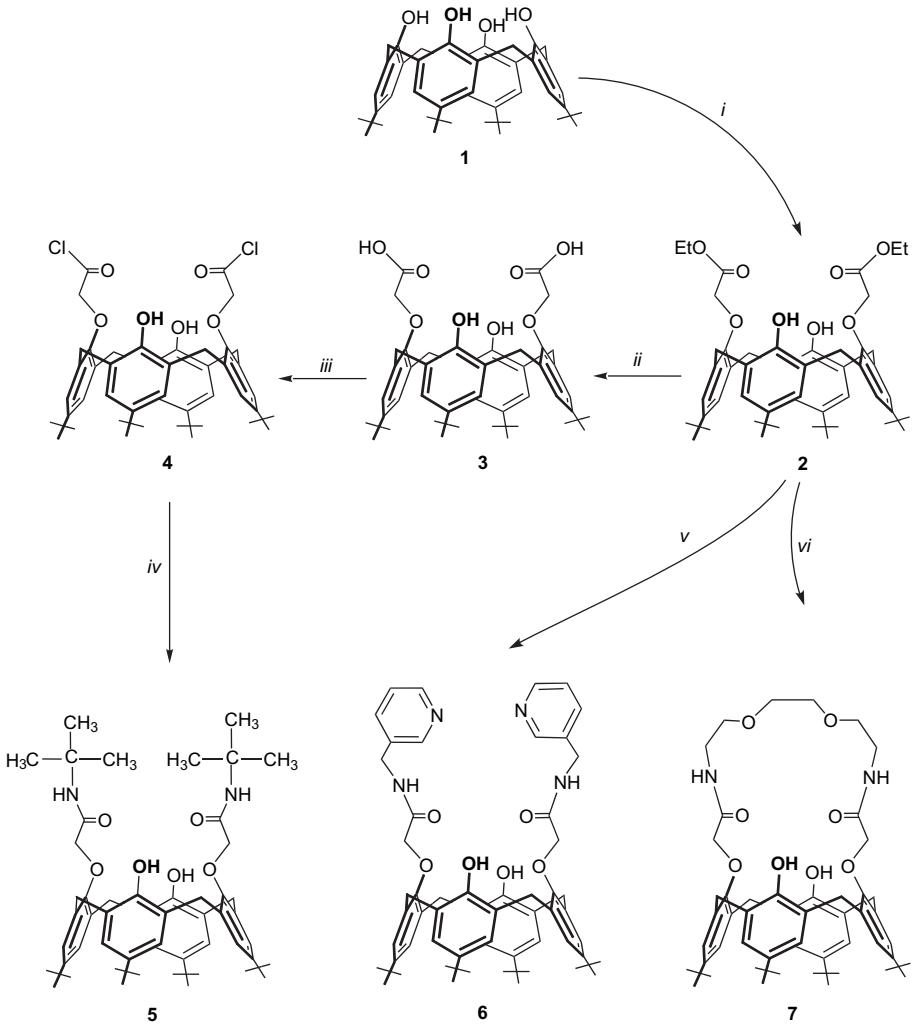
($Cr_2O_7^{2-}$/$HCr_2O_7^-$) binding properties of *p-tert*-butylcalix[4]arene ionophores bearing different diamide functions, which have often been claimed to act as binding sites in the complexation of dichromate anions.

2. Results and discussion

2.1. Synthesis

In this work, we extend our previous studies and explore the binding properties of *p-tert*-butylcalix[4]arene diamide derivatives (**5**–**7**) bearing different binding sites toward dichromate anions. The synthetic route for the preparation of *p-tert*-butylcalix[4]arene diamide derivatives is described in Scheme 1. For the synthesis of these *p-tert*-butylcalix[4]-arene diamides, the parent compounds **1**–**4** and **7** were prepared according to published procedures.[23,24] Two synthetic methods, aminolysis[25] and acid chloride methods,[23] were tried for the synthesis of compound **5**. In aminolysis, no any amide derivatives could be obtained, maybe due to steric hindrance of the amine derivative. Therefore, we tried an acid chloride method to synthesize compound **5**. This time, from the reaction of acid chloride **4** with *tert*-butyl amine we obtained *p-tert*-butylcalix[4]arene diamide **5** in 87% yield. 5,11,17,23-*tert*-Butyl-25,27-ethoxycarbonyl-methoxy-26,28-hydroxycalix[4]arene (**2**) was heated at reflux with 3-aminomethylpyridine and 3,6-dioxa-1,8-diamino octane to give the corresponding diamide derivatives of *p-tert*-butylcalix[4]arene (**6** and **7**) in 73% and 56% yields, respectively. A mixture of toluene–methanol (1:1) was employed as toluene facilitates the dissolution of diester, while methanol is beneficial in transforming the ethyl ester to the more reactive methyl ester prior to aminolysis.[25]

The diamide derivatives **5**–**7** were characterized by a combination of FTIR, ^{1}H NMR, FABMS, and elemental analysis. The formation of the diamide derivatives of *p-tert*-butylcalix[4]arene (**5**–**7**) was confirmed by the appearance of the characteristic amide bands at about 1680 cm^{-1} and also by the disappearance of ester carbonyl band at 1755 cm^{-1} in the IR spectra. The conformational characteristics of calix[4]arenes were conveniently estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^{1}H NMR spectrum.[26,27] ^{1}H NMR spectroscopic data showed that compounds **5**–**7** were in the cone conformation.



Scheme 1. (i) Ethylbromoacetate, K_2CO_3, acetone; (ii) NaOH, ethanol; (iii) oxalyl dichloride, THF, pyridine; (iv) *tert*-butyl amine, THF, pyridine; (v) 3-amino-methylpyridine, toluene–methanol; (vi) 3,6-dioxa-1,8-diamino octane, toluene–methanol.

A typical AX pattern was observed for the methylene bridge $ArCH_2Ar$ protons at δ 3.39 and 4.11 ppm (J=13.4 and 13.3 Hz, respectively) for **5**, δ 3.27 and 3.84 ppm (J= 13.3 Hz) for **6**, and δ 3.28 and 4.12 ppm (J=13.5 Hz) for **7** in ^{1}H NMR. The high field doublets at δ 3.39 ppm for **5**, δ 3.27 ppm for **6**, and δ 3.28 ppm for **7** were assigned to the equatorial protons of methylene groups, whereas the low field signals at δ 4.11 ppm for **5**, δ 3.84 ppm for **6**, and δ 4.12 ppm for **7** were assigned to the axial protons in the ^{1}H NMR.

2.2. Extraction studies

Dichromate anions are important because of their high toxicity and presence in soils and waters.[23] 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 amide, amino, and nitrile on their lower rim are efficient extractants for oxoanions.[20,21,28–31] We were interested in synthesizing *p-tert*-butylcalix[4]arene diamide derivatives containing different binding sites in the cone conformation, and examining their extraction properties for dichromate ions. The present work determines the strategic requirements for two-phase extraction measurements. A preliminary evaluation of the extraction efficiencies of **5**–**7** has been carried out by solvent extraction of $Na_2Cr_2O_7$ from water into dichloromethane at the pH range of 1.5–4.5. The results are summarized in Table 1.

The extraction data (Table 1, Figs. 1 and 2) showed that the diamide derivatives **6** and **7** were effective extractants for the extraction of dichromate anions at low pH while the extraction yield by **5** was negligible. The percentage of dichromate anions extracted was 24.8 for **6** and 64.4 for **7** when the pH of the aqueous solution was 1.5, and they attained minimum <1.0 for **6** and 35.1 for **7** when pH of the aqueous solution increased to 4.5. *p-tert*-Butylcalix[4]arene diamide derivative **6** provides suitable binding sites for dichromate anions at low pH due to the presence of protonable amine moieties. Therefore, an anion-switchable complex is formed in the two-phase extraction system (Scheme 2),

Table 1. Percentage extraction of dichromate by extractants **5**–**7** at different pH values[a,b]

Compound	pH			
	1.5	2.5	3.5	4.5
5	<1.0	<1.0	<1.0	<1.0
6	24.8±0.3	11.5±0.2	10.3±0.3	<1.0
7	64.4±0.2	60.2±0.1	55.0±0.3	35.1±0.2

[a] Averages and standard deviations calculated for data obtained from three independent extraction experiments.
[b] Aqueous phase, [metal dichromate]=1×10^{-4} M; organic phase, dichloromethane, [ligand]=1×10^{-3} M at 25 °C, for 1 h.

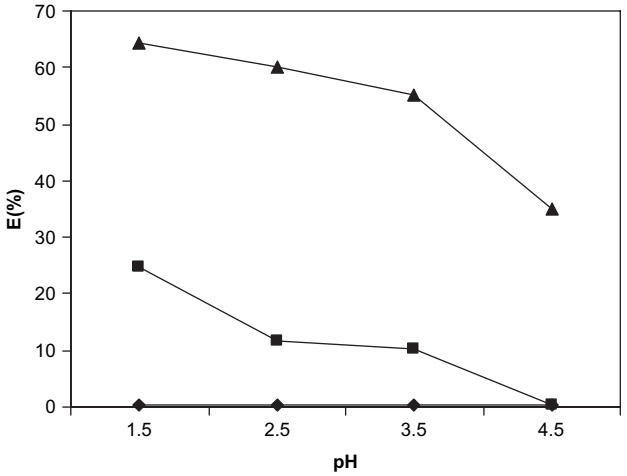


Figure 1. Plots of extraction (E%) versus pH following the two-phase solvent extraction of dichromate anion with compounds **5**–**7**.

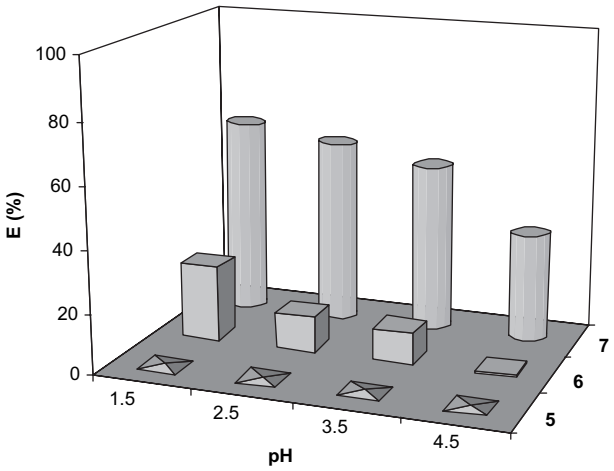
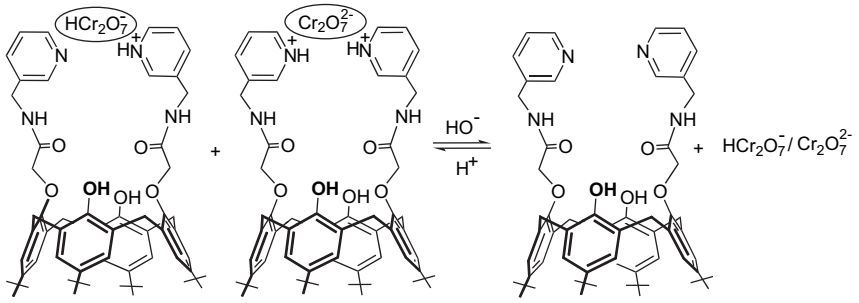


Figure 2. Extraction percentages of dichromate anion with **5**–**7** at pH 1.5–4.5.



Scheme 2. The proposed interactions of compound **6** with dichromate anions.

because of the proton transfer to the nitrogen atom of the amine unit in **6**. This also reflects the fact that the complex with dichromate ions is more stable in low pH medium. According to our knowledge the increase in extraction efficiency of **7** can be attributed to a number of reasons. Compound **7** possesses an amide nitrogen, carbonyl, and oxa oxygen, facilitating hydrogen bonding with the dichromate anion. The next reason is that **7** has a more stable structure because of the bridging of the two amide moieties by a 1,8-dioxa octyl unit. Therefore, one reason that the extraction ability of **6** is less than that of **7**, maybe that **6** has a more flexible structure. Another reason is that the amide oxygen can be protonated[32] at low pH, although this is more difficult than in **6**. This also implies a decrease in extraction efficiency of **7** with increasing pH of the solution, due to the fact that protonation decreases, especially at pH 4.5. Consequently, all these causes can cooperatively contribute to the higher extraction efficiency of **7** over **6**. On the other hand, the ineffectiveness of **5** can be attributed to steric hindrance by its bulky groups.

All these data have been analyzed using the classical slope analysis method.[23] Figure 3 represents the extractions into dichloromethane at different concentrations of **6** and **7** for the dichromate anion. A linear relationship between log *D* versus log[*L*] is observed with a slope for dichromate by **6** and **7**, which equals 1.07 and 1.25 at pH 1.5, respectively, suggesting that **6** and **7** form 1:1 complexes with dichromate anions.

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(VI) form, and pK_{a1} and pK_{a2} values of these equations are 0.74 and 6.49, respectively. It is apparent to us that the ligands **6** and **7** form complexes mostly with $HCr_2O_7^-$ ion. This as well as the explanations above have allowed us to consider these

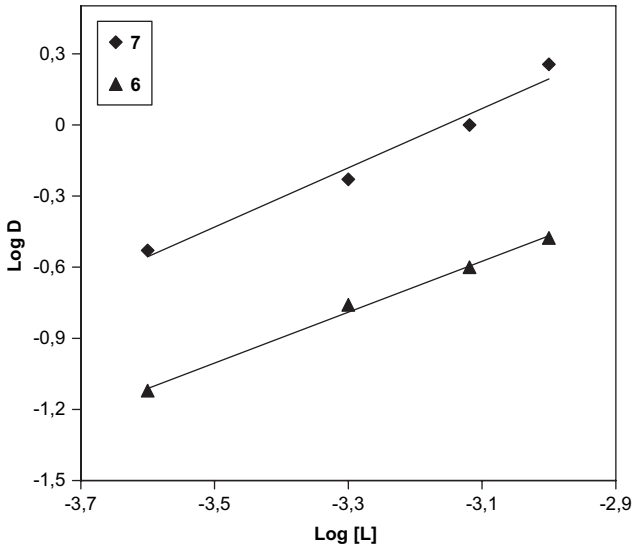
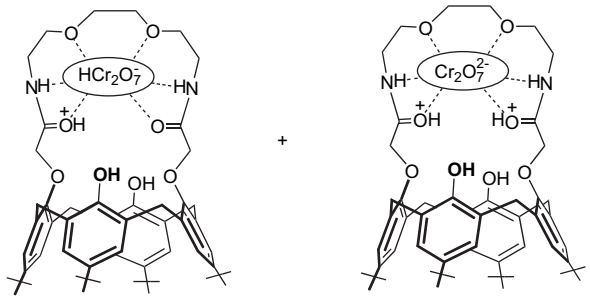


Figure 3. Log *D* versus log[*L*] for the extraction of dichromate anions by the ligands **6** and **7** from an aqueous phase into dichloromethane at 25 °C.



Scheme 3. The proposed interactions of compound **7** with dichromate anions.

simultaneous extractions of 1:1 (Eqs. 1 and 2) complexes according to the following equilibria (Schemes 2 and 3):

$$LH^+_{(org)} + HCr_2O^-_{7(aq)} \overset{\log K_{ex}}{\rightleftharpoons} \lfloor LH^+(HCr_2O_7^-)\rfloor_{(org)} \quad (1)$$

$$LH^{2+}_{2(org)} + Cr_2O^{2-}_{7(aq)} \overset{\log K'_{ex}}{\rightleftharpoons} \lfloor LH_2^{2+}(Cr_2O_7^{2-})\rfloor_{(org)} \quad (2)$$

According to these assumptions, the extraction constants (K_{ex}) have been calculated from the experimental data. Calculations of these constant values lead to $\log K_{ex} = \log K'_{ex} = 2.74 \pm 0.2$ for **6** and $\log K_{ex} = \log K'_{ex} = 3.96 \pm 0.2$ for **7**.

3. Conclusions

In conclusion, the synthesis and dichromate anion extraction ability of *p-tert*-butylcalix[4]arene based receptors **5–7** were studied. The spectroscopic data indicated that the diamide compounds (**5–7**) are in the cone conformation. The dichromate anion complexation studies showed that compounds **6** and **7** were effective receptors while compound **5** was not useful for $Cr_2O_7^{2-}/HCr_2O_7^-$ anions. The extraction efficiency of **7** was much higher than that of **6**. It could be concluded that the complexation of $Cr_2O_7^{2-}/HCr_2O_7^-$ anions depends on the structural properties of the receptor such as hydrogen binding ability, stability or rigidity, and protonation ability. The calixarene based receptors could be proved to find remarkable applications in the design of chemical sensors, using electrochemical transduction/as conventional ion selective electrodes (ISE) and solid-state sensors (ISFETs).

4. Experimental

4.1. General

Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were obtained on a Perkin–Elmer 1605 FTIR spectrometer using KBr pellets. UV–visible spectra were obtained on a Shimadzu 160A UV–visible 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 F_{254} on aluminum). Flash chromatography separations were performed on a Merck silica gel 60 (230–400 mesh). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Aldrich, and used without further purification. Toluene was distilled from CaH_2 and stored over sodium wire. Other commercial grade solvents were distilled, and then stored over molecular sieves. Anions were used as their sodium salts. The drying agent employed was anhydrous $MgSO_4$. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

4.2. Synthesis

Compounds **1**–**4** and **7** were synthesized according to previously described methods.[23,24] The synthesis of the other compounds **5** and **6** was firstly reported in this study.

4.2.1. Synthesis of *p-tert*-butylcalix[4]arene diamide 5. 5,11,17,23-*tert*-Butyl-25,27-bis(chlorocarbonylmethoxy)-26,28-hydroxycalix[4]arene **4** (6.2 g, 5.44 mmol) was dissolved in dry THF (100 mL). The addition of pyridine (1 mL) and the solution of *tert*-butyl amine (3.3 mL, 31 mmol) in THF (25 mL) was made sequentially and added dropwise over about 1 h with continuous stirring at room temperature. The reaction mixture was then stirred and heated at reflux for 5 h, after which most of the solvent was distilled off in vacuo. The residue was diluted with water (200 mL) and neutralized by 0.1 M HCl. The solid material was then filtered and washed with 2 M HCl, $NaHCO_3$, and distilled water sequentially. Recrystallization of residue from ethanol furnished **5** (4.14 g, 87%) as white crystals, mp 287 °C. [Found: C, 77.01; H, 9.07; N, 3.27. $C_{56}H_{78}N_2O_6$ requires: C, 76.84; H, 8.98; N, 3.20%.] ν_{max} (KBr pellet): 3470, 3379, 1683 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 0.94 (18H, s, ^{t}Bu), 1.30 (18H, s, ^{t}Bu), 1.51 (18H, s, ^{t}Bu), 3.39 (4H, d, *J* 13.4 Hz, $ArCH_2Ar$), 4.11 (4H, d, *J* 13.3 Hz, $ArCH_2Ar$), 4.43 (4H, s, OCH_2), 6.80 (4H, s, Ar*H*), 7.01 (2H, s, OH), 7.09 (4H, s, Ar*H*), 8.31 (2H, s, NH); FABMS *m*/*z*: $[M+Na]^+$, found: 898.2.

4.2.2. Synthesis of *p-tert*-butylcalix[4]arene diamide 6. 3-Aminomethylpyridine (20.0 mmol) was dissolved in a 1:1 toluene–MeOH mixture (60 mL) and added dropwise to a solution of 5,11,17,23-*tert*-butyl-25,27-ethoxycarbonylmethoxy-26,28-hydroxycalix[4]arene **2** (4.0 mmol) in toluene (20 mL) with continuous stirring at room temperature for about 30 min. Then the reaction mixture was heated at reflux and the reactions were monitored by TLC. After the substrate had been consumed the solvent was evaporated under reduced pressure and the residue was triturated with MeOH to give *p-tert*-butylcalix[4]arene diamide **6**, the crude product was purified by flash chromatography (SiO_2, EtOAc–*n*-hexane 3:1) and recrystallized from CH_2Cl_2–MeOH to give **6** (2.76, 73%) as white crystals; mp 248 °C. [Found: C, 76.31; H, 7.74; N, 5.83. $C_{60}H_{72}O_6N_4$ requires: C, 76.23; H, 7.68; N, 5.93%.] ν_{max} (KBr pellet): 3454, 3358, 1685 cm^{-1}; δ_H (400 MHz $CDCl_3$): 0.91 (18H, s, ^{t}Bu), 1.19 (18H, s, ^{t}Bu), 3.27 (4H, d, *J* 13.3 Hz, $ArCH_2Ar$), 3.84 (4H, d, *J* 13.3 Hz, $ArCH_2Ar$), 4.46–4.48 (8H, m, OCH_2, Ar–CH_2–NH), 6.77 (4H, s, Ar*H*), 6.94 (4H, s, ArH), 7.04–7.07 (2H, m, Py*H*), 7.18 (2H, s, OH), 7.56 (2H, d, *J* 7.8 Hz, Py*H*), 8.40 (2H, d, *J* 4.5 Hz, Py*H*), 8.55 (2H, d, Py*H*), 9.10 (2H, t, NH); FABMS *m*/*z*: $[M+Na]^+$, found: 968.2.

5. Analytical procedure

The dichromate anion extraction experiments of *p-tert*-butylcalix[4]arene diamide derivatives **5**–**7** were performed following Pedersen's procedure.[33] An aqueous solution of sodium dichromate (10 mL of a 1×10^{-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 1×10^{-3} M) in CH_2Cl_2 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 dichromate ion remaining in the aqueous phase was then determined spectrophotometrically as described previously.[23] Blank experiments showed that no dichromate extraction occurred in the absence of calix[4]arene. The percentage 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:

$$E\% = [(A_0 - A/A_0)] \times 100 \quad (3)$$

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

Acknowledgements

We thank the Scientific and Technical Research Council of Turkey (TUBITAK-Grant Number TBAG-104T199) and Research Foundation of Selçuk University, Konya, Turkey for financial support of this work.

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