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Synthesis of two calix[4]arene diamide derivatives for extraction of chromium(VI)

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Abstract—The synthesis of four diamide derivatives of the *p-tert*-butylcalix[4]arenes from the reaction of 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **2** with various primary amines were reported. The ^{1}H and ^{13}C NMR, data showed that the synthesized compounds exist in the cone conformation. The complexing properties of these compounds toward $Cr_2O_7^{2-}/HCr_2O_7^{-}$ anions are also studied. It has been observed that receptors **5** and **6** are better extractant than the compounds **3** and **4**. The protonated alkyl ammonium form of **5** and **6** is an effective extractant for transferring $HCr_2O_7^{-}/Cr_2O_7^{2-}$ anions from an aqueous phase into a dichloromethane layer.

1. Introduction

Much attention has been paid in recent years to chemical separation techniques that involve the design and synthesis of new extraction reagents for metal ions. This attention results in part from environmental concerns, efforts to save energy, and recycling at the industrial level. In this respect, supramolecular chemistry has provided solutions in the search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they delineate a suitable binding site.[1]

Calixarenes are a family of cyclic oligomers prepared from formaldehyde and *para*-substituted phenols via cyclic condensation under alkaline conditions. It was suggested that the calixarenes could be regarded as the third generation of supramolecules, after crowns and cyclodextrins.[1,2] These phenol-based macrocycles have proven to be excellent ligands for the formation of stable complexes with cations, anions, or neutral molecules.[3]

The molecular recognition of anionic guest species by positively charged or electron deficient neutral abiotic receptor molecules is an area of intense current interest. The importance of favorable amine, amide, or imide (–NH_2/OC–NH/OC═N) 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. Several studies on anion coordination have reported using calixarene based chelating units.[4–10] For example, a few excellent approaches emphasized by Beer et al.[5] regarding calixarene based anion receptors, and the work highlighted by Gale[6] for anion and ion-pair receptor chemistry are complimentary studies in the field of anion coordination. Among anions, chromate and dichromate anions are important because of their high toxicity,[9a,b] and also because of their presence in soils and waters.[9c] Chromium(VI) is a carcinogen in humans and animals, with chromates and dichromates being both mutagenic and genotoxic. 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 target and damage DNA.[9d] Chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) are dianions with oxide functionalities at their periphery. Nevertheless, since the periphery of the anions has oxide moieties, these are potential sites for hydrogen bonding to the host molecule. Recently we have demonstrated that the amine base derivatives of calix[4]arenes are very effective toward chromate and dichromate anions.[6–10] The main focus of this work is the design of new calixarene-based ionophores that effectively bind anions and can be useful for multiple applications such as laboratory, clinical, environmental, and industrial process analysis. In our previous work,[10] we have extended the field of research of design structures based on a calix[4]arene platform for the extraction of dichromate anions. Herein, we report synthesis and extraction studies of new designed calix[4]arene platform with alkyl amide derivatives on their lower rim.

Keywords: Calix[4]arene; Dichromate anions; Solvent extraction; Diamide.
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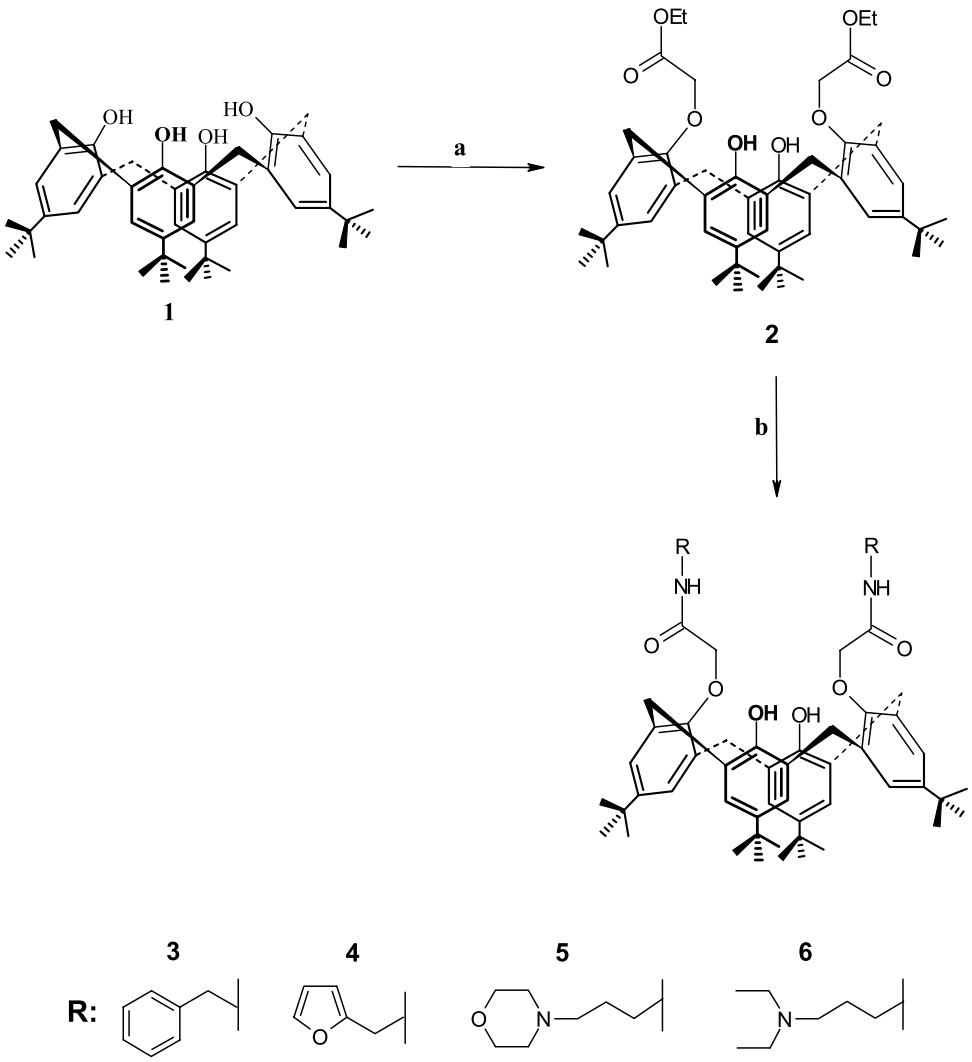
2. Results and discussion

2.1. Design and synthesis of the new hosts

In this work, we extend our previous studies and explore the binding properties of calix[4]arene amide derivatives **3–6** towards anions such as dichromate. To achieve the desired goal, *p-tert*-butylcalix[4]arene **1** was chosen as the precursor.[11] A synthetic scheme was developed to enable its derivatization: the synthetic route is depicted in Scheme 1. The synthesis of compounds **1** and **2** is based on previously published procedures,[12] compounds **4–6** are reported for the first time while compound **3** was previously obtained from the acid chloride derivative of calix[4]-arene.[10d] In the synthesis of calix[4]arene amides, the aminolysis reaction of calix[4]arene esters is a new facile method.[13] Therefore, following the strategy outlined in Scheme 1; 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **2** was refluxed with, respectively, benzyl amine, furfuryl amine, 3-morpholino propyl amine and 3-ethylamino-1-propyl amine in toluene/MeOH (1:2) mixture to give corresponding amide derivatives of *p-tert*-butyl calix[4]arene **3–6** in 75–80% yield.

The new compounds **3–6** were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, FAB-MS, and elemental analysis. The formation of diamide derivatives of calix[4]arene **3–6** was confirmed by the appearance of the characteristic amide bands at about 1684 cm^{-1} in their IR spectra, and 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 and ^{13}C NMR spectroscopy.[1]

^{1}H and ^{13}C NMR data showed that compounds **3–6** have a cone conformation. A typical AB pattern was observed for the methylene bridge $ArCH_2Ar$ protons at 3.19 and 3.72 ppm (J=13.4 Hz) for **3**, 3.30 and 3.91 ppm (J=13.3 Hz) for **4**, 3.35 and 4.04 ppm (J=13.3 Hz) for **5** and 3.32 and 4.05 ppm (J=13.2 Hz) for **6** in ^{1}H NMR and two signals covering a range of δ 31.63 and 30.98 ppm in ^{13}C NMR. The high field doublets at 3.19 ppm for **3**, 3.30 ppm for **4**, 3.35 ppm for **5** and 3.32 ppm for **6** were assigned to the equatorial protons of methylene groups, whereas the low field signals at 3.72 ppm for **3**, 3.91 ppm for **4**, 4.04 ppm for **5** and 4.05 ppm for **6** were assigned to the axial protons in the ^{1}H NMR.



Scheme 1. (a) K_2CO_3/acetone, EtBrOAc, reflux, 24 h; (b) Primary amine, MeOH/toluene (1:1), reflux.

2.2. Two-phase solvent extraction

Chromate and dichromate anions are important because of their high toxicity[9b] and their presence in soils and waters.[9a,c] 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 chromate and dichromate ($Cr_2O_7^{2-}$/$HCr_2O_7^-$) ions are dianions where the periphery of the anions have oxide moeties. It is known that calix[4]arenes with amino functionalities on their lower rim are efficient extractants for oxoanions.[8b,c,10a,b] These oxides alter potential sites for hydrogen bonding to the host molecule.

We were interested in synthesizing new calix[4]arene diamide derivatives in the cone conformation and to 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 **3**–**6** has been carried out by solvent extraction of $Na_2Cr_2O_7$ from water into dichloromethane at different pH values. The results are summarized in Table 1.

Table 1. Percentage extraction of dichromate by extractants **3**, **4**, **5** and **6** at different pH values[a]

	Dichromate anion extracted (%)			
	PH			
Compound	1.5	2.5	3.5	4.5
3	8.2	3.1	3.7	3.6
4	6.1	<0.1	1.0	1.0
5	35.9	23.5	2.1	1.3
6	[b]	87.8	81.6	19.0

[a] Aqueous phase, [metal dichromate]=1×10^{-4} M; organic phase, dichloromethane, [ligand]=1×10^{-3} M or solid phase [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]×100.
[b] Partly soluble at this pH.

From the extraction data (Fig. 1), the percentage of dichromate extracted increased by lowering the pH of the aqueous phase. This pH dependence can be explained by anion hydration. 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 than does the 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. For the calix[4]arene amides **5** and **6** we discount the possibility that increased extraction at lower pH values when compared to **3** and **4**, is due to protonation of the amine nitrogens.

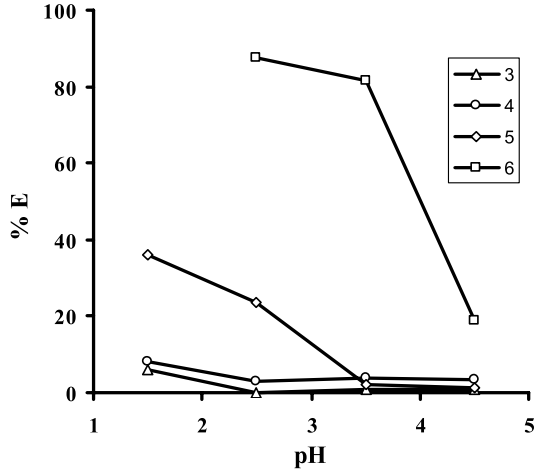


Figure 1. Plots of extraction (*E*%) versus pH following the two phase solvent extraction of dichromate with compounds **3**, **4**, **5** and **6**.

Because the pK_a of protonated amides (R-C(OH^+)NH_2) is approximately −1, the protonated form of calix[4]arene amid derivatives **3** and **4** are not expected to be present in significant concentration in aqueous solutions having pH values in the 1.5–4.5 range.

By contrast, amines **5** and **6** are expected to be protonated in these acidic aqueous solutions (generally the pK_a of protonated amines is around 10–11).

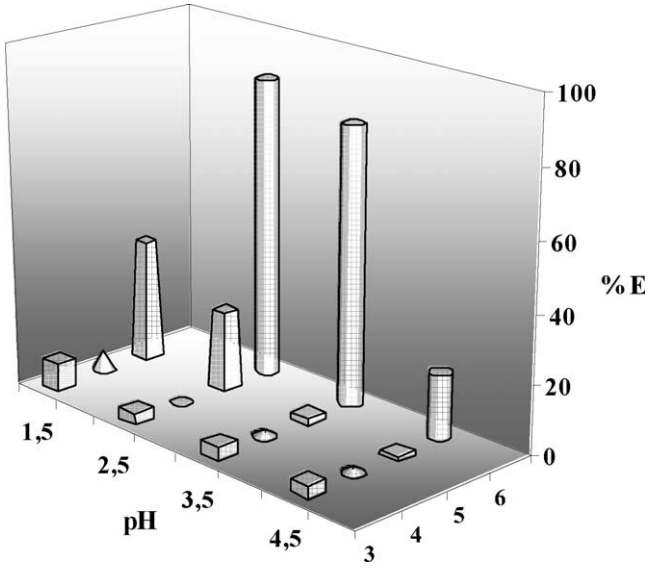
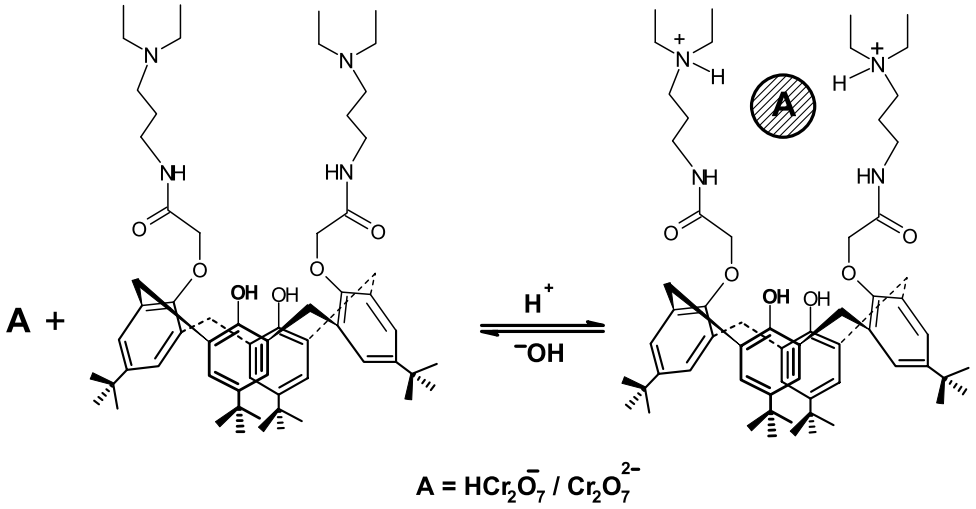


Figure 2. Extraction percentrage of dichromate anions with **3**, **4**, **5** and **6** at pH 1.5–4.5.

The extraction data (Fig. 2) showed that the extractant **6** is more effective for the extraction of dichromate anions at low pH (1.5–4.5) because **5** and **6** contains a protonable amine binding site appropriate for anion binding at low pH. Therefore, it can be demonstrated that because of the proton transfer to the nitrogen atom of the amine unit in **5** and **6**, protonated 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 reversible process (Scheme 2).

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



Scheme 2. The proposed interactions of compound **6** with $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ ions.

equilibrium:

$$n(LH^{n+})_{org} + nA_{aq}^{n-} \rightleftharpoons ((LH^{n+})_n, A_n^{n-})_{org} \quad (1)$$

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

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

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 s[*L*]lope that allows for the determination of the stoichiometry of the extracted species, where is defined as the analytical concentration of the ligand in the organic phase. Figure 3 exhibits the extraction into dichloromethane at different concentrations of **5** and **6** 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 **5** and **6** being approximately equal to 1 (at pH 1.5 for ligand **5** and at pH 2.5 for ligand **6**), suggesting that these ligands **5** and **6** form 1:1 complexes with the dichromate anion.

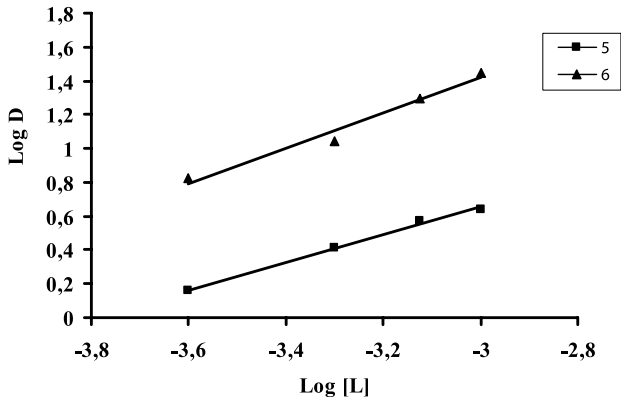


Figure 3. Log *D* versus log[*L*] for the extraction of dichromate by the ligand **5** and **6** from an aqueous phase into dichloromethane at 25 °C.

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 pK_{a_1} and pK_{a_2} values of these equations are 0.74 and 6.49, respectively. It is apparent to us that the ligands **5** and **6** form complex mostly with $HCr_2O_7^-$ ion. This has allowed us to consider that mostly the Eqs. 4 and 5 this simultaneous extraction of 1:1 complexes according to the following equilibria:

$$(LH^+)_{org} + HCr_2O_{7aq}^- \overset{K_{ex}}{\rightleftharpoons} (LH^+, HCr_2O_7^-)_{org} \quad (4)$$

$$(LH_2^{2+})_{org} + Cr_2O_{7aq}^{2-} \overset{K'_{ex}}{\rightleftharpoons} (LH_2^{2+}, Cr_2O_7^{2-})_{org} \quad (5)$$

According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} and $K_{ex}{}'$ values using Eq. 3. Calculations of these constant values lead to $\log K_{ex} = \log K_{ex}{}' = 3.12 \pm 0.2$ for **5** and $\log K_{ex} = \log K_{ex}{}' = 4.58 \pm 0.2$ for **6**.

3. Conclusion

In conclusion, the synthesis and complexation ability of four calix[4]arene based receptors **3–6** were studied. The spectroscopic data indicated that these compounds (**3–6**) adopt the cone conformation. The complexation studies show that compounds **5** and **6** are better receptors for $Cr_2O_7^{2-}/HCr_2O_7^-$ anions compared with **3** and **4**. Morever, the extraction properties of **5** and **6** are enhanced in the acidic medium for $Cr_2O_7^{2-}/HCr_2O_7^-$ anions due to their protonation from the extraction phenomenon it could be concluded that the complexation of $Cr_2O_7^{2-}/HCr_2O_7^-$ depend on the nature and aggregation of the ions round the receptor. This is a particularly important feature if it is desirable to recover the particular metal in pure form and

reuse the extractant. The calixarene based receptors could be proved to find remarkable applications in the design of chemical sensors, using an electrochemical transduction/as conventional ion selective electrodes (ISE) and solid-state sensors (ISFETs).

4. Experimental

Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^{1}H and ^{13}C 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–vis spectra were obtained on a Shimadzu 160A UV–vis spectrophotometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. A Crison MicropH 2002 digital 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. Compounds **1** and **2** were synthesized according to previously described methods.[12]

4.1. Analytical procedure

The dichromate anion extraction experiments of calix[4] arene daimide derivatives **3**, **4**, **5** and **6** were studied by liquid–liquid extraction experiments following Pedersen's procedure.[14] Into a vial was pipetted an aqueous solution (10 mL) containing 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.[10b] 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:

$$(E\%) = \frac{A_0 - A}{A_0} \times 100$$

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

4.2. General procedure for the synthesis of compound 3, 4, 5 and 6

An appropriate primary amine (20.0 mmol) was dissolved in 1:2 toluene/MeOH mixture (60 mL) and added dropwise to a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **2** (4.0 mmol) in 20 mL toluene with continuous stirring at room temperature for about 30 min. Then the reaction mixture was refluxed 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 a crude product. The crude products were purified by flash chromatography (SiO_2, CH_2Cl_2/Hexane 2:1) and recrystallized from CH_2Cl_2/MeOH.

4.2.1. Compound 3. White crystals; yield 79%; mp 248–250 °C; IR (KBr): 3353 (OH), 1684 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.80 (t, 2H, N*H*), 7.21 (s, 2H, O*H*), 7.18 (m, 10H, Ar*H*), 6.93 (s, 4H, Ar*H*), 6.72 (s, 4H, Ar*H*), 4.45 (d, 4H, NHCH_2), 4.29 (s, 4H, OCH_2CO), 3.72 (d, 4H, $J=13.4$ Hz, ArCH_2Ar), 3.19 (d, 4H, $J=13.4$ Hz, ArCH_2Ar), 1.20 (s, 18H, C(CH_3)$_3$), 0.88 (s, 18H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$): δ 167.91 (*C*=O), 149.29, 148.96, 148.12, 142.68, 136.87, 128.94, 128.53, 127.54, 126.79, 126.99, 125.32, 125.00, 123.24 (Ar*C*), 96.20 (*C*(CH$_3$)$_3$), 77.28, 76.96 (O*C*H$_2$), 76.64, 74.65 (NH*C*H$_2$), 31.70, 30.93 (Ar*C*H$_2$Ar); FAB-MS *m/z*: (966.4) $[M+Na]^+$. Anal. Calcd for $C_{62}H_{74}N_2O_6$ (943.3): C, 78.95%; H, 7.91%; N, 2.97%. Found: C, 78.68%; H, 7.76%; N, 2.86%.

4.2.2. Compound 4. White crystals; yield 78%; mp 289–291 °C; IR (KBr): 3326 (OH), 1684 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.01 (t, 2H, N*H*), 7.22 (d, 2H, O*H*), 7.10 (d, 2H, Ar*H*), 7.01 (s, 4H, Ar*H*), 6.82 (s, 4H, Ar*H*, ph), 6.23 (s, 4H, Ar*H*, ph), 4.54 (d, 4H, NHCH_2), 4.45 (s, 4H, OCH_2CO), 3.91 (d, 4H, $J=13.3$ Hz, ArCH_2Ar), 3.30 (d, 4H, $J=13.3$ Hz, ArCH_2Ar), 1.21 (s, 18H, C(CH_3)$_3$), 0.96 (s, 18H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$): δ 167.79 (*C*=O), 149.41, 148.83, 148.02, 142.79, 137.05, 132.28, 128.61, 128.23, 127.83, 126.94, 126.10, (Ar*C*), 96.22 (*C*(CH$_3$)$_3$), 77.32, 76.88 (O*C*H$_2$), 76.56, 74.64 (NH*C*H$_2$), 31.74, 30.91 (Ar*C*H$_2$Ar); FAB-MS *m/z*: (946.1) $[M+Na]^+$. Anal. Calcd for $C_{58}H_{70}N_2O_8$ (923.2): C, 75.46%; H, 7.64%; N, 3.03%. Found: C, 75.69; H, 7.27%; N, 3.23%.

4.2.3. Compound 5. White crystals; yield 76%; mp 244–246 °C; IR (KBr): 3351 (OH), 1686 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.87 (t, 2H, N*H*), 7.79 (s, 2H, O*H*), 7.00 (s, 4H, Ar*H*), 6.86 (s, 4H, Ar*H*), 4.50 (s, 4H, OCH_2CO), 4.04 (d, 4H, $J=13.3$ Hz, ArCH_2Ar), 3.54 (b, 8H, OCH_2CH$_2$N), 3.36–3.41 (m, 4H, NHCH_2CH$_2$CH$_2$N), 3.35 (d, 4H, $J=13.3$ Hz, ArCH_2Ar), 2.18 (m, 8H, NCH_2CH$_2$O), 2.30 (m, 4H, NHCH$_2$CH$_2$CH_2N), 1.75 (b, 4H, NHCH$_2$CH_2CH$_2$N), 1.19 (s, 18H, C(CH_3)$_3$), 0.97 (s, 18H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$): δ 167.82 (*C*=O), 149.38, 148.65, 148.57, 143.34, 132.22, 127.06, 126.24, 125.62 (Ar*C*), 96.16 (*C*(CH$_3$)$_3$), 77.25 (O*C*H$_2$), 76.93 (NH*C*H$_2$CH$_2$CH$_2$N),

76.62 ($NHCH_2CH_2CH_2N$), 74.83 ($NHCH_2CH_2CH_2N$), 56.27 (OCH_2CH_2N), 53.58 (OCH_2CH_2N), 31.63, 30.97 ($ArCH_2Ar$); FAB-MS *m/z*: (1040.4) $[M+Na]^+$. Anal. Calcd for $C_{62}H_{88}N_2O_8$ (1017.41): C, 73.19%; H, 8.72%; N, 5.51%. Found: C, 73.38%; H, 8.66%; N, 5.40%.

4.2.4. Compound 6. White crystals; yield 78%; mp 179–180 °C; IR (KBr): 3353 (OH), 1684 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.76 (t, 2H, N*H*), 7.62 (s, 2H, O*H*), 7.00 (s, 4H, Ar*H*), 6.83 (s, 4H, Ar*H*), 4.48 (s, 4H, OCH_2CO), 4.05 (d, 4H, $J=13.2$ Hz, $ArCH_2Ar$), 3.42 (q, 4H, $NHCH_2CH_2CH_2N$), 3.32 (d, 4H, $J=13.2$ Hz, $ArCH_2Ar$), 2.35 (t, 4H, $NHCH_2CH_2CH_2N$), 2.28 (q, 8H, NCH_2CH_3), 1.66 (p, 4H, $NHCH_2CH_2CH_2N$), 1.18 (s, 18H, $C(CH_3)_3$), 0.96 (s, 18H, $C(CH_3)_3$), 0.81 (t, 12H, NCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 167.70 (*C*=O), 149.40, 148.77, 148.40, 143.13, 132.30, 127.14, 126.17, 125.57 (Ar*C*), 96.16 ($C(CH_3)_3$), 77.25 (OCH_2), 76.93 ($NHCH_2CH_2CH_2N$), 76.62 ($NHCH_2CH_2CH_2N$), 74.84 ($NHCH_2CH_2CH_2N$), 50.84, 46.70 (CH_3CH_2N), 31.63, 30.98 ($ArCH_2Ar$), 11.65 (CH_3CH_2N); FAB-MS *m/z*: (1012.5) $[M+Na]^+$. Anal. Calcd for $C_{62}H_{92}N_4O_6$ (989.45): C, 75.26%; H, 9.37%; N, 5.66%. Found: C, 75.12%; H, 9.48%; N, 5.72%.

Acknowledgements

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