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Tetrahedron
Tetrahedron 63 (2007) 5076–5082

Synthesis and lead(II) sorption of silica gel-immobilized, di-ionizable calix[4]arenes

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Received 11 January 2007; revised 13 March 2007; accepted 16 March 2007
Available online 21 March 2007

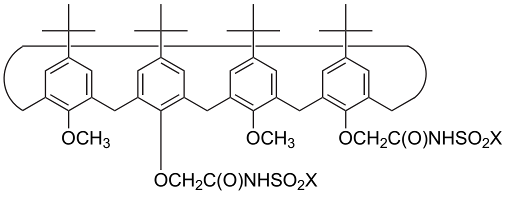
Abstract—Di-ionizable calix[4]arenes with two lower-rim *N*-(X)sulfonyl carboxamide groups were covalently linked to silica gel via a single attachment on the upper rim. Both the acidity of the ionizable groups (X group variation) and the length of the spacer that joins the ligands to the silica gel matrix were varied. Preliminary evaluation of these new ion-exchange resins for sorption of lead(II) from aqueous solutions was conducted.

1. Introduction

Calixarenes are one of the most important platforms for the preparation of new macrocyclic hosts for complexation of neutral and ionic guest species.[1–5] We have synthesized and evaluated novel di-ionizable calix[4]arenes with two acidic groups attached via the phenolic oxygens on the lower rim.[6–11] Such ligands are efficient agents for extraction of divalent metal ions from aqueous solutions into organic solvents by an ion-exchange mechanism in which the di-ionized ligand and the complexed metal ion form electroneutral complexes. This avoids the need to extract an anion from the aqueous phase into the organic medium and is especially important for potential practical applications in which the aqueous phase anions are highly hydrophilic chloride, nitrate, and sulfate.

To provide ligands with 'tunable' acidity, we have attached *N*-(X)sulfonyl carboxamide functions to the lower rim of calix[4]arenes.[6–11] Variation of the electron-withdrawing properties of X changes the acidity of the ligand.

We have reported efficient extraction of Pb^{2+} and Hg^{2+} from acidic aqueous solutions into chloroform by di-ionizable calix[4]arenes **1** with high selectivity over alkali and alkaline earth metal ions, as well as other transition and heavy metal cations (Fig. 1).[6,7] To explore the behavior of such ligands in ion-exchange chromatography, their immobilization on a polymeric support is required.



($X = CH_3$, C_6H_5, C_6H_4-4-NO_2, CF_3)

Figure 1. Di-ionizable calix[4]arene ligands with high extraction propensity for Pb^{2+} and Hg^{2+}.

Recently, the topic of polymer-appended calixarenes as ion carriers was reviewed.[12] Only a few studies of calixarene immobilization on silica gel have appeared in the literature. Glennon and co-workers were the first to bind calix[4]arene ligands to silica gel.[13–15] In their work, an upper-rim attachment site was present on each of the four aromatic units of the calix[4]arene. Other workers have bound a calix[4]arene-crown ether to silica gel via two upper-rim attachment sites.[16] In both cases, the multiple attachments will restrict the conformational mobility of the calix[4]arene units. Since we have demonstrated that conformationally mobile di-ionizable calix[4]arenes provide more selective metal ion complexation than conformationally locked analogues,[10] our objective was to utilize a single linkage to bind the upper rim of our ligands to silica gel.

We now report the synthesis of novel ion-exchange resins **2**–**10** (Fig. 2) in which the di-ionizable calix[4]arene units are connected to silica gel by a single, upper-rim linkage. Results from preliminary studies of Pb^{2+} sorption from aqueous solutions are also presented. To our knowledge, this is the

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Keywords: Functionalized calix[4]arenes; Ion-exchange resins; Heavy metal sorption.

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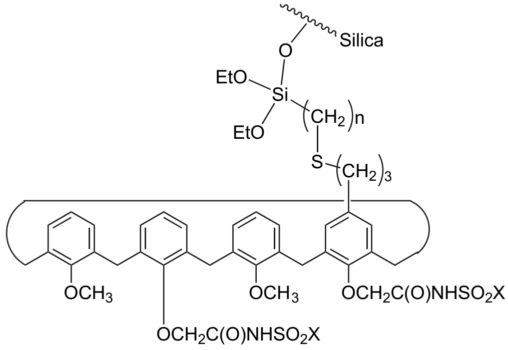
doi:10.1016/j.tet.2007.03.104



n	X	
3	CH_3	**2**
3	C_6H_5	**3**
3	C_6H_4-4-NO_2	**4**
6	CH_3	**5**
6	C_6H_5	**6**
6	C_6H_4-4-NO_2	**7**
10	CH_3	**8**
10	C_6H_5	**9**
10	C_6H_4-4-NO_2	**10**

Figure 2. Di-ionizable calix[4]arenes ligands bound to silica gel.

first reported immobilization of a proton-ionizable calixarene on silica gel.

2. Results and discussion

2.1. Synthesis of functionalized calixarenes

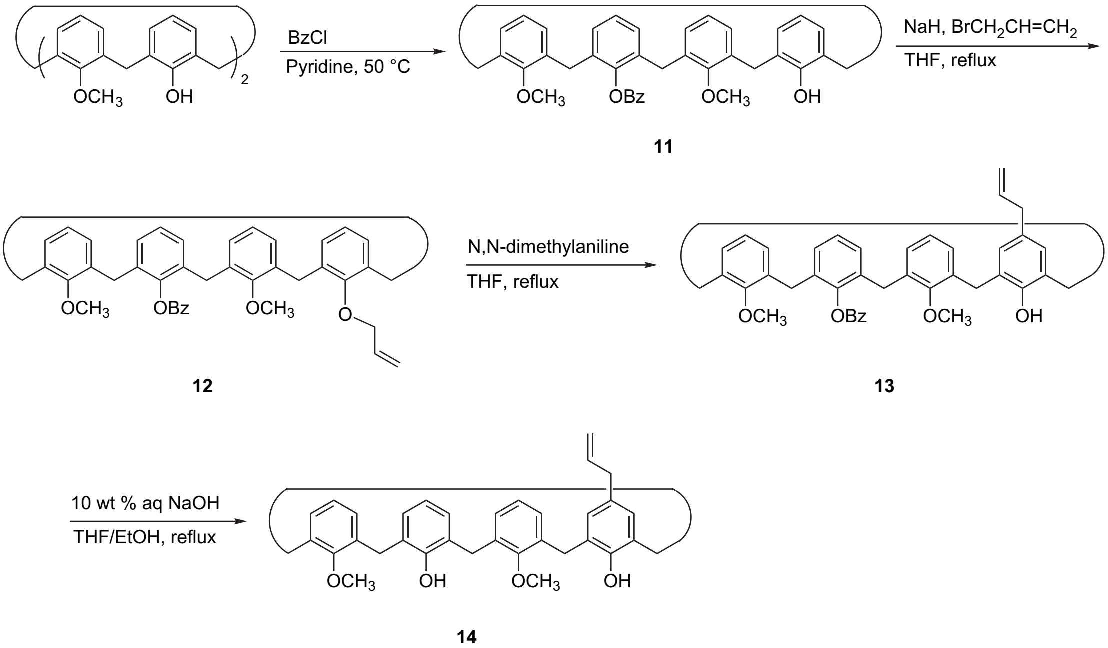
Synthesis of the dimethylated calix[4]arene with a single allyl substituent on the upper rim involved a total of four reactions (Scheme 1). Monoprotection of one hydroxyl group on 25,27-dimethoxy-26,28-dihydroxycalix[4]arene was carried out with excess benzoyl chloride and pyridine using a modified method based on the literature.[17] Several trial reactions were performed to determine the optimal conditions for obtaining monobenzoyl-protected calix[4]arene **11** (Table 1). The best result was achieved when the calixarene was treated with 8 equiv of benzoyl chloride at 50 °C overnight. When the reaction was repeated under these conditions on larger scale, a 73% yield of **11** was obtained.

Reaction of 25,27-dimethoxy-26-benzoyloxy-28-hydroxyloxycalix[4]arene (**11**) with NaH and allyl bromide in THF afforded 25,27-dimethoxy-26-benzoyloxy-28-(2′-propenyl)-oxycalix[4]arene (**12**) in 88% yield. Claisen rearrangement of **12** in refluxing *N*,*N*-dimethylaniline[18] gave 5-(2′-propenyl)-25,27-dimethoxy-26-benzoyloxy-28-(2′-propenyl)oxycalix[4]arene (**13**) in 97% yield. Hydrolysis of ester **13** with aqueous NaOH in EtOH–THF gave **14** in 82% yield.[17] The ^{1}H NMR spectra of compounds **11**–**14** revealed that all were conformationally mobile in $CDCl_3$.

Preparation of the di-ionizable calix[4]arene precursors is illustrated in Scheme 2. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (**14**) was treated with NaH and ethyl bromoacetate to give 5-(2′-propenyl)-25,27-dimethoxy-26,28-di[(ethoxycarbonyl)methoxy]calix[4]arene (**15**) in 78% yield. Diester **15** was hydrolyzed with Me_4NOH in aqueous THF to give diacid **16** in 92% yield. Diacid **16** was then converted into the corresponding di(acid chloride) by reaction with oxalyl chloride in benzene. Reaction of the di(acid chloride) with four different sulfonamide anions gave the target di-ionizable calix[4]arenes **17**–**20** in high yields.

2.2. Linker synthesis

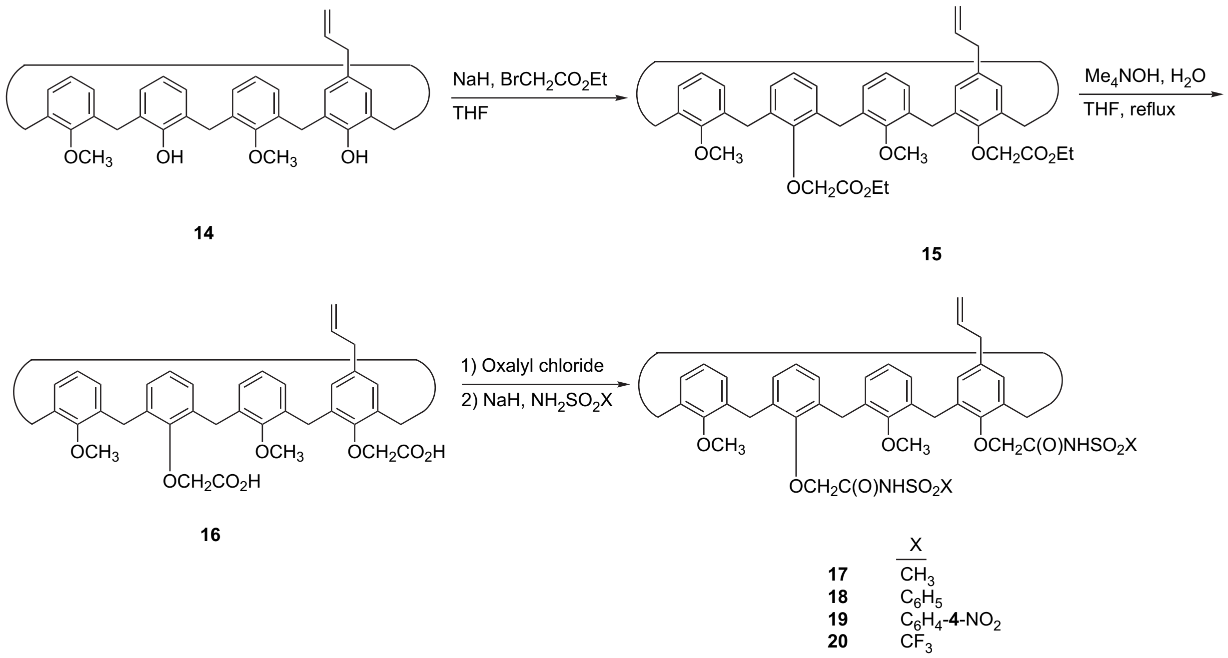
The length of the spacer that separates the di-ionizable calix[4]arene unit from the silica gel matrix was systematically varied. In addition to commercially available



Scheme 1. Synthesis of 5-(2′-propenyl)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (**14**).

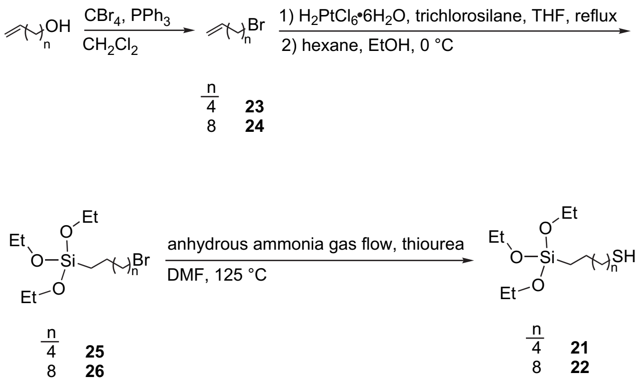
Table 1. Optimization of reaction conditions for monoprotection of calix[4]arene **11**

Entry	1	2	3	4	5
Reaction temperature	rt	rt	50 °C	rt	50 °C
BzCl (equiv)	1.1	4	4	8	8
BzCl (equiv) for second addition	17	4	8	4	0
Reaction after 48 h	Complete	Incomplete	Complete	Incomplete	Complete
Starting material recovered	0	42%	0	56%	0
Monobenzoylated product	38%	15%	44%	20%	73%
Dibenzoylated product	26%	Trace	40%	Trace	12%



Scheme 2. Preparation of di-ionizable calix[4]arene ligands.

3-mercaptopropyltriethoxysilane, 6-mercaptohexyltriethoxysilane (**21**) and 10-mercaptodecyltriethoxysilane (**22**) were needed. Compounds **21** and **22** were synthesized following a literature method[19] (Scheme 3). Commercially available 9-decen-1-ol and 5-hexen-1-ol were reacted with CBr_4 and PPh_3 to give 10-bromodecene (**23**) and 6-bromohexene (**24**), respectively. The starting material and solvent had to be scrupulously dry for clean conversions. ω-Bromoalk-1-enes **23** and **24** were reacted with trichlorosilane and hexachloroplatinic acid in THF at reflux and then treated with cold ethanol in hexane to give ω-triethoxysilylalkyl bromides **25** and **26** in yields over 70% after distillation under reduced pressure. ω-Triethoxysilylalkyl bromides **25** and **26** were treated with thiourea in DMF with an anhydrous ammonia gas flow at 125 °C for 5 h to give ω-triethoxysilylalkyl mercaptans **21** and **22** in 30–40% yields after distillation under reduced pressure.



Scheme 3. Synthesis of ω-triethoxysilylalkyl mercaptans **21** and **22**.

2.3. Immobilization of di-ionizable calix[4]arenes on silica gel

Immobilization of calix[4]arenes **17**–**20** with a single allyl group on the upper rim on silica gel was achieved through reaction of the allyl group with ω-triethoxysilylalkyl mercaptan and cumene hydroperoxide (CHP) catalyst in 1,2-dichloroethane by radical addition and then refluxing the product with activated silica gel.[13,15] Combustion analysis of the immobilized silica gel for nitrogen was performed to determine the ligand loading. Following reactions of di-ionizable calix[4]arene **20** with the three linkers and then with silica gel, no nitrogen was detected in the product resins. This reveals cleavage of the ionizable groups under the conditions of immobilization.

2.4. Metal ion sorption by new ion-exchange resins

Initial probing of the complexation ability by the new ion-exchange resins **2**–**10** was conducted with Pb^{2+} sorption

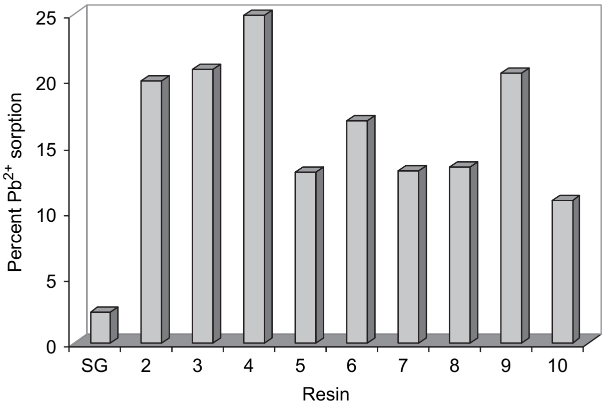


Figure 3. Percent Pb^{2+} sorption by unfunctionalized silica gel (SG) and by di-ionizable calix[4]arenes **2**–**10** immobilized on silica gel.

from aqueous solutions at pH 5.3. A 1.00-g sample of the resin was packed in a 42 mm ID Tefzel column. Through the resin bed was passed a dilute aqueous solution of $Pb(NO_3)_2$ of such concentration that there was a 1:1 ratio of calixarene units in the resin bed and Pb^{2+} in solution. After loading with the sample solution, the column was rinsed with DI water to remove any unbound metal ions. The sorbed Pb^{2+} ions were then eluted from the column with dilute HNO_3 and their concentration in the eluant was determined by atomic absorption spectrophotometry. The percentage of Pb^{2+} ions in the sample solution that were sorbed by the ion-exchange resin was then calculated.

Results for Pb^{2+} sorption by silica gel itself and by new ion-exchange resins **2**–**10** containing immobilized di-ionizable calix[4]arene ligands are presented in Figure 3. There was little sorption of Pb^{2+} by a column of silica gel itself. For resins **2**–**10**, the percent Pb^{2+} sorption values are in the range of 10–25% depending upon the length of the spacer and the identity of X in the di-ionizable calix[4]arene unit. In general, resins **2**–**4** with the shortest spacer (n=3) gave higher levels of Pb^{2+} sorption than did resins **5**–**7** with intermediate spacer length (n=6) or resins **8**–**10** with the longest spacer length (n=10). For variation of the X in resins **2**–**4** with the shortest spacer length, Pb^{2+} sorption was significantly higher for the more strongly electron-withdrawing 4-nitrophenyl group than for the phenyl and methyl groups. Thus, the more acidic di-ionizable calix[4]arene ligand unit gave the highest Pb^{2+} sorption. However, with the intermediate and longest spacers, the highest Pb^{2+} sorption levels were observed with X=phenyl than with X=methyl or 4-nitrophenyl.

Further studies on the influence of structural variations in the organic portions of the new ion-exchange resins on their metal ion sorption behaviors are in progress and the results will be reported in due course.

3. Experimental

3.1. General

Melting points were determined with a Mel-Temp melting point apparatus. Infrared (IR) spectra were recorded with a Perkin–Elmer Model 1600 FTIR spectrometer as deposits from CH_2Cl_2 solution on a NaCl plate. The ^1H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FTNMR (^1H 500 MHz and ^{13}C 126 MHz) spectrometer in $CDCl_3$ with Me_4Si as an internal standard, unless mentioned otherwise. Chemical shifts (δ) are given in parts per million downfield from TMS and coupling constants (J) values are in hertz. A Shimadzu Model 6300 atomic absorption spectrophotometer was used for the Pb^{2+} analysis. The pH was measured with a Fisher Accumet AR25 pH meter with a microcombination electrode. Elemental analysis was performed by Desert Analytics Laboratory of Tucson, Arizona.

3.2. Synthesis

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Tetrahydrofuran (THF) was dried over sodium with benzophenone as indicator and distilled just before use. 25,27-Dimethoxycalix[4]arene was prepared by a reported method.[20] 6-Bromohex-1-ene (**23**),[21] 10-bromodec-1-ene (**24**),[19] 6-triethoxysilylhexyl bromide (**25**),[22] 10-triethoxysilyldecyl bromide (**26**),[19] and 10-triethoxysilyldecyl mercaptan (**22**)[19] were synthesized by literature methods. Silica gel (Mallinckrodt SiliCAR®, 60–200 mesh) was activated by heating at 150 °C under oil pump vacuum overnight.

3.2.1. 25,27-Dimethoxy-26-benzoyloxy-28-hydroxycalix[4]arene (11). Into pyridine (30 mL), 25,27-dimethoxycalix[4]arene (1.36 g, 3.0 mmol) was added followed by BzCl (2.8 mL, 24 mmol). The solution was stirred at 50 °C overnight. Dilute HCl (300 mL) was added to produce a white solid, which was filtered and recrystallized from $CHCl_3$ with slow addition of MeOH to yield a white solid (9.07 g, 73%) with mp 287–288 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3301 (O–H), 1721 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.75 (s, 6H, OCH_3), 2.82–4.20 (m, 8H, $ArCH_2$), 6.20–7.43 (m, 18H, ArH, OH); ^{13}C NMR ($CDCl_3$): δ 30.7, 37.4, 61.1, 118.8, 123.8, 125.3, 127.5, 128.1, 128.3, 128.4, 129.6, 130.8, 132.3, 132.8, 133.1, 147.8, 153.1, 155.5, 163.9. Anal. Calcd for $C_{37}H_{32}O_5$: C, 79.83; H, 5.79. Found: C, 79.79; H, 5.81%.

3.2.2. 25,27-Dimethoxy-26-benzoyloxy-28-(2′-propenyl)-oxycalix[4]arene (12). To a suspension of NaH (0.14 g, 5.83 mmol) in THF (20 mL) was added a solution of **11** (1.00 g, 1.80 mmol) in THF (20 mL). After stirring for 30 min, allyl bromide (0.44 g, 3.6 mmol) was added and the mixture was refluxed overnight. The excess NaH was destroyed by careful addition of water and the organic solvent was evaporated in vacuo. To the residue, CH_2Cl_2 (50 mL) was added and the organic layer was washed with 1 N HCl (30 mL) and then with brine (30 mL), dried over $MgSO_4$, and evaporated in vacuo to afford a white solid (0.71 g, 60%) with mp 202–205 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1727 (C=O), 1587 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.63 (s, 6H, OCH_3), 2.66–4.25 (m, 12H, $ArCH_2$), 4.87–4.98 (m, 2H, $CH{=}CH_2$), 5.49–5.60 (m, 1H, $CH{=}CH_2$), 6.27–7.58 (m, 17H, ArH); ^{13}C NMR ($CDCl_3$): δ 30.8, 37.0, 59.9, 74.1, 112.6, 122.2, 123.1, 127.7, 129.0, 130.3, 131.6, 132.3, 133.2, 133.4, 133.8, 136.9, 138.2, 156.0, 156.8, 164.4. Anal. Calcd for $C_{40}H_{36}O_5$: C, 80.51; H, 6.08. Found: C, 80.77; H, 6.24%.

3.2.3. 5-(2′-Propenyl)-25,27-dimethoxy-26-benzoyloxy-28-hydroxycalix[4]arene (13). A solution of **12** (1.00 g, 1.68 mmol) in *N*,*N*-dimethylaniline (10 mL) was refluxed for 3 h. The mixture was allowed to cool and then poured into a 1:1 mixture of concentrated HCl–ice (150 mL). The precipitate was taken up in CH_2Cl_2 (100 mL) and the organic layer was washed with 6 N HCl (3×50 mL), water (50 mL), and brine (50 mL), dried over $MgSO_4$, and evaporated in vacuo. Recrystallization of the residue from CH_2Cl_2–MeOH gave a white solid (0.97 g, 97%) with mp 244–246 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3337 (OH), 1733 (C=O), 1638 (C=C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.74 (s, 6H, OCH_3), 4.32–2.18 (m, 10H, $ArCH_2Ar$, $ArCH_2O$), 5.17–5.08 (m, 2H, $CH=CH_2$), 5.98–6.12 (m, 1H, $CH=CH_2$), 7.67–6.16 (m, 17H, ArH); ^{13}C NMR ($CDCl_3$): δ 30.75, 37.41, 39.53, 61.06, 115.12, 123.79, 125.27, 127.45, 127.99, 128.38, 128.45, 128.50, 128.98, 129.39, 129.54, 129.62, 129.94, 130.84, 132.32, 132.80, 133.08, 133.16, 138.45, 147.77, 151.36, 155.48, 163.86. Anal. Calcd for $C_{40}H_{36}O_5$: C, 80.51; H, 6.08. Found: C, 80.92; H, 6.13%.

3.2.4. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (14). To **13** (1.00 g, 1.68 mmol) was added 50 mL each of 10% NaOH, EtOH, and THF and the mixture was refluxed overnight. After adding 5% HCl, the precipitate was filtered and dissolved in CH_2Cl_2 (100 mL). The solution was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. Recrystallization of the residue from CH_2Cl_2–MeOH gave a white solid (0.68 g, 82%) with mp 242–243 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3284 (OH), 1642 (C=C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.27 (d, J=7.0 Hz, 2H, $CH_2CH=CH_2$), 3.95 (s, 6H, OCH_3), 3.37 (d, J=13.0 Hz, 2H, $ArCH_2$), 4.28 (d, J=13.0 Hz, 2H, $ArCH_2$), 3.39 (d, J=13.0 Hz, 2H, $ArCH_2$), 4.30 (d, J=13.0 Hz, 2H, $ArCH_2$), 4.98–5.12 (m, 2H, $CH=CH_2$), 5.88–6.02 (m, 1H, $CH=CH_2$), 6.67 (t, J=7.5 Hz, 1H, ArH), 6.73 (t, J=7.5 Hz, 2H, ArH), 6.87 (d, J=7.5 Hz, 6H, ArH), 7.05 (d, J=8.0 Hz, 2H, ArH), 7.63 (s, 1H, OH), 7.75 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 31.1, 31.2, 39.4, 63.6, 115.2, 119.1, 125.3, 128.0, 128.1, 128.5, 129.0, 130.3, 132.9, 133.0, 138.2, 151.3, 153.0, 153.2, 166.6. Anal. Calcd for $C_{33}H_{32}O_4$: C, 80.46; H, 6.55. Found: C, 80.28; H, 6.76%.

3.2.5. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-di[(ethoxycarbonyl)methoxy]calix[4]arene (15). A solution of **14** (1.00 g, 2.0 mmol) in THF (30 mL) was added dropwise to a suspension of NaH (0.20 g, 8.3 mmol) in THF (5 mL). After stirring for 2 h, ethyl bromoacetate (2.03 g, 12.2 mmol) was added and the mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue was dissolved in CH_2Cl_2. The solution was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. Chromatography on silica gel with hexanes–EtOAc (17:3) as eluant gave a colorless oil (1.04 g, 78%). IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1762 (C=O), 1644 (C=C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.32 (t, J=7.0 Hz, 6H, CH_3), 2.68–4.48 (m, 24H, $ArCH_2$, $CH_2CH=CH_2$, OCH_2CO, CH_2CH_3, OCH_3), 4.48–5.55 (m, 2H, $CH=CH_2$), 5.39–5.81 (m, 1H, $CH=CH_2$), 6.00–7.43 (m, 11H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.22, 30.7, 60.9, 114.7, 122.5, 127.5, 128.3, 128.7, 128.9, 132.9, 133.1, 133.4, 133.8, 136.7, 136.8, 138.0, 153.4, 155.8, 158.1, 159.0, 169.4. Anal. Calcd for $C_{41}H_{44}O_8$: C, 74.08; H, 6.67. Found: C, 73.79; H, 6.86%.

3.2.6. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-bis(carboxymethoxy)calix[4]arene (16). A solution of **15** (5.00 g, 7.53 mmol) in THF (100 mL) and 10% aq Me_4NOH (100 mL) was refluxed overnight, and the THF was evaporated in vacuo. To the residue, CH_2Cl_2 was added and the organic layer was separated and washed with 5% HCl until pH 1 and then with brine, dried over $MgSO_4$, and evaporated in vacuo to give a white solid (4.23 g, 92%) with mp 93–97 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3169 (OH), 1761 (C=O), 1640 (C=C), 1203 and 1053 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.42–3.27 (m, 2H, $CH_2CH=CH_2$), 3.33 (d, J=13.0 Hz, 2H, $ArCH_2$), 3.84 (s, 6H, OCH_3), 4.25 (d, J=13.0 Hz, 2H, $ArCH_2$), 3.37 (d, J=13.5 Hz, 2H, $ArCH_2$), 4.28 (d, J=13.5 Hz, 2H, $ArCH_2$), 4.70 (d, J=10.0 Hz, 4H, CH_2CO_2H), 5.00–5.15 (m, 2H, $CH=CH_2$), 5.91–6.05 (m, 1H, $CH=CH_2$), 6.48–6.62 (m, 6H, ArH), 6.97 (s, 2H, ArH), 7.02 (t, J=7.5 Hz, 1H, ArH), 7.19 (d, J=7.5 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 30.7, 39.4, 53.4, 63.8, 72.1, 116.0, 124.9, 128.7, 129.5, 132.6, 135.0, 137.3, 153.0, 154.1, 155.8, 169.7. Anal. Calcd for $C_{37}H_{36}O_8 \cdot 0.1CH_2Cl_2$: C, 72.20; H, 5.91. Found: C, 72.08; H, 6.23%.

3.2.7. General procedure for synthesis of 5-(2′-propenyl)-25,27-dimethoxy-26,28-di[*N*-(X)sulfonyl carbamoylmethoxy]calix[4]arenes 17–20. Oxalyl chloride (1.39 mL, 16.3 mmol) was added to **16** (1.00 g, 1.63 mmol) in benzene (50 mL). The mixture was refluxed for 6 h and the solvent was evaporated in vacuo to give the di(acid chloride). The appropriate sulfonamide (4.0 mmol) in THF (5 mL) was added to NaH (0.38 g, 16.3 mmol) in THF (20 mL) and the mixture was stirred at room temperature for 2 h. The di(acid chloride) was added and the mixture was stirred overnight. The excess NaH was destroyed with careful addition of water. The THF was evaporated and the residue was washed with dilute HCl until pH 1 and the mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated in vacuo.

3.2.7.1. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-di(*N*-methanesulfonyl carbamoylmethoxy)calix[4]arene (17). Compound **17** was obtained as white solid (1.18 g, 95%) with mp 105–110 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3341 (NH), 1730 (C=O), 1642 (C=C), 1350 (S=O), 1146 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.08–5.18 (m, 28H, $CH=CH_2$, $ArCH_2$, OCH_3, $CH_2CH=CH_2$, CH_3), 5.79–7.22 (m, 12H, ArH, $CH=CH_2$), 8.80–8.97 (s, 2H, NH); ^{13}C NMR ($CDCl_3$): δ 31.1, 36.8, 39.0, 41.5, 58.1, 64.0, 71.1, 115.8, 123.9, 126.0, 128.8, 129.7, 131.1, 132.5, 135.0, 151.4, 152.9, 158.0, 168.2, 169.8. Anal. Calcd for $C_{39}H_{42}N_2S_2O_{10} \cdot 0.5C_6H_6$: C, 62.90; H, 5.66; N, 3.49. Found: C, 62.96; H, 5.38; N, 3.22%.

3.2.7.2. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-di(*N*-benzenesulfonyl carbamoylmethoxy)calix[4]arene (18). Compound **18** was obtained as white solid (1.31 g, 90%) with mp 75–77 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3324 (NH), 1733 (C=O), 1636 (C=C), 1349 (S=O), 1154 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.83–5.18 (m, 22H, $CH=CH_2$, $ArCH_2$, OCH_3, $CH_2CH=CH_2$, OCH_2), 5.62–5.84 (br s, 1H, $CH=CH_2$), 6.07–8.38 (m, 21H, ArH), 9.18–9.32 (s, 2H, NH); ^{13}C NMR ($CDCl_3$): δ 25.6, 30.7, 39.0, 39.2, 53.4, 68.0, 71.7, 115.4, 123.6, 126.4, 128.6, 129.1, 129.2, 132.8, 134.3, 134.5, 135.2, 137.6, 138.5, 141.9, 151.0, 152.6, 166.3. Anal. Calcd for $C_{49}H_{46}N_2S_2O_{10}$: C, 66.35; H, 5.23; N, 3.16. Found: C, 66.01; H, 5.11; N, 3.34%.

3.2.7.3. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-di[*N*-(4-nitrobenzene)sulfonyl carbamoylmethoxy]calix[4]arene (19). Compound **19** was obtained as a yellow solid (1.55 g, 96%) with mp 100–105 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3326 (NH), 1735 (C=O), 1642 (C=C), 1350 (S=O), 1165 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.02–5.17 (m, 22H, $CH{=}CH_2$, $ArCH_2$, OCH_3, $CH_2CH{=}CH_2$, OCH_2), 5.68–6.04 (m, 1H, $CH{=}CH_2$), 6.32–7.38 (m, 11H, ArH), 8.12–8.58 (m, 8H, ArH), 9.41–9.57 (br s, 2H, NH); ^{13}C NMR ($CDCl_3$) δ 25.6, 30.8, 38.8, 53.4, 68.0, 70.9, 123.5, 123.9, 124.4, 127.9, 128.7, 129.4, 129.7, 130.2, 130.6, 132.7, 134.8, 135.3, 137.5, 144.1, 147.5, 151.0. Anal. Calcd for $C_{49}H_{44}N_4S_2O_{14}\cdot 0.2C_6H_6$: C, 60.74; H, 4.59; N, 5.64. Found: C, 60.98; H, 4.57; N, 5.54%.

3.2.7.4. 5-(2′-Propenyl)-25,27-dimethoxy-26,28-di(*N*-trifluoromethanesulfonyl carbamoylmethoxy)calix[4]arene (20). Compound **20** was obtained as a white solid (1.30 g, 93%) with mp 115–117 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 3200 (NH), 1739 (C=O), 1640 (C=C), 1388 (S=O), 1198 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.84–5.14 (m, 22H, $CH{=}CH_2$, $ArCH_2$, OCH_3, $CH_2CH{=}CH_2$, OCH_2), 6.27–7.24 (m, 11H, ArH), 5.70–6.04 (br s, 1H, $CH{=}CH_2$), 8.63–9.89 (s, 2H, NH); ^{13}C NMR ($CDCl_3$): δ 30.3, 30.8, 38.9, 39.1, 53.4, 58.6, 68.0, 71.1, 115.6, 117.8, 120.4, 124.1, 128.7, 129.7, 130.2, 131.1, 132.6, 135.2, 137.5, 150.8, 152.5, 158.0, 165.8. Anal. Calcd for $C_{39}H_{36}N_2F_6S_2O_{10}$: C, 53.79; H, 4.17; N, 3.22. Found: C, 53.66; H, 3.98; N, 2.99%.

3.2.8. 6-Triethoxysilylhexyl mercaptan (21). A stream of anhydrous ammonia gas was slowly introduced into a mixture of 6-triethoxysilylhexyl bromide (**25**) (26.20 mmol), thiourea (2.39 g, 31.57 mmol), and DMF (1.68 mL). While the ammonia flow was maintained, the mixture was heated at 125 °C for 5 h with stirring. Filtration followed by concentration of the filtrate in vacuo gave an oil, which was distilled under reduced pressure (3.10 g, 59%) with bp 88 °C/0.5 mmHg. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 2590 (SH), 1082 (Si–O), 1106 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.63 (t, J=8.0 Hz, 2H, CH_2Si), 1.23 (t, J=7.0 Hz, 9H, CH_3), 1.31–1.42 (m, 7H, SH, CH_2), 1.57–1.64 (m, 2H, CH_2CH_2SH), 2.49–2.58 (m, 2H, CH_2SH), 3.79–3.84 (m, 6H, OCH_2); ^{13}C NMR ($CDCl_3$): δ 10.34, 18.29, 22.66, 24.63, 27.98, 32.52, 33.92, 58.29, 70.25. Anal. Calcd for $C_{12}H_{28}SSiO_3\cdot 0.5H_2O$: C, 49.82; H, 9.69. Found: C, 49.85; H, 9.66%.

3.2.9. General procedure for immobilization of proton-ionizable calix[4]arenes on silica gel. The di-ionizable calix[4]arenes **19**–**22** (2.20 mmol) were reacted with ω-triethoxysilylalkyl mercaptan (2.20 mmol) in the presence of CHP in $ClCH_2CH_2Cl$ (5 mL) at 70 °C overnight. Activated silica gel (10.00 g) in toluene (40 mL) was added and mixture was refluxed for 72 h. The mixture was cooled to room temperature and filtered. The functionalized silica gel was washed with 50 mL each of toluene, acetone, and MeOH, and then dried in oven for 1 h.

3.2.9.1. 25,27-Dimethoxy-26,28-di(*N*-methanesulfonyl carbamoylmethoxy)calix[4]arene immobilized by a dipropyl sulfide linkage on silica gel. Resin **2** was obtained as a cream-colored solid. Elemental analysis: C, 6.64; H, 1.07; N, 0.22%. Ion-exchange capacity=78 μmol of ligand/g of resin.

3.2.9.2. 25,27-Dimethoxy-26,28-di(*N*-benzenesulfonyl carbamoylmethoxy)calix[4]arene immobilized by a dipropyl sulfide linkage on silica gel. Resin **3** was obtained as a cream-colored solid. Elemental analysis: C, 8.97; H, 1.22; N, 0.33%. Ion-exchange capacity=118 μmol of ligand/g of resin.

3.2.9.3. 25,27-Dimethoxy-26,28-di[*N*-(4-nitrobenzene)-sulfonyl carbamoylmethoxy]calix[4]arene immobilized by a dipropyl sulfide linkage on silica gel. Resin **4** was obtained as a cream-colored solid. Elemental analysis: C, 3.19; H, 0.72; N, 0.15%. Ion-exchange capacity=54 μmol of ligand/g of resin.

3.2.9.4. 25,27-Dimethoxy-26,28-di(*N*-methanesulfonyl carbamoylmethoxy)calix[4]arene immobilized by a propylhexylsulfide linkage on silica gel. Resin **5** was obtained as a cream-colored solid. Elemental analysis: C, 4.19; H, 0.83; N, 0.17%. Ion-exchange capacity=61 μmol of ligand/g of resin.

3.2.9.5. 25,27-Dimethoxy-26,28-di(*N*-benzenesulfonyl carbamoylmethoxy)calix[4]arene immobilized by a propylhexylsulfide linkage on silica gel. Resin **6** was obtained as a cream-colored solid. Elemental analysis: C, 9.53; H, 1.08; N, 0.37%. Ion-exchange capacity=132 μmol of ligand/g of resin.

3.2.9.6. 25,27-Dimethoxy-26,28-di[*N*-(4-nitrobenzene)-sulfonyl carbamoylmethoxy]calix[4]arene by a propylhexylsulfide linkage on silica gel (7). Resin **7** was obtained as a cream-colored solid. Elemental analysis: C, 6.25; H, 0.91; N, 0.27%. Ion-exchange capacity=96 μmol of ligand/g of resin.

3.2.9.7. 25,27-Dimethoxy-26,28-di(*N*-methanesulfonyl carbamoylmethoxy)calix[4]arene immobilized by a propyldecylsulfide linkage on silica gel (8). Resin **8** was obtained as a cream-colored solid. Elemental analysis: C, 9.37; H, 1.45; N, 0.53%. Ion-exchange capacity=189 μmol of ligand/g of resin.

3.2.9.8. 25,27-Dimethoxy-26,28-di(*N*-benzenesulfonyl carbamoylmethoxy)calix[4]arene immobilized by a propyldecylsulphide linkage on silica gel. Resin **9** was obtained as a cream-colored solid. Elemental analysis: C, 9.24; H, 1.48; N, 0.36%. Ion-exchange capacity=128 μmol of ligand/g of resin.

3.2.9.9. 25,27-Dimethoxy-26,28-di[*N*-(4-nitrobenzene)-sulfonyl carbamoylmethoxy]calix[4]arene immobilized by a propyldecylsulfide linkage on silica gel. Resin **10**

was obtained as a cream-colored solid. Elemental analysis: C, 9.38; H, 1.25; N, 0.62%. Ion-exchange capacity= 221 μmol of ligand/g of resin.

3.3. Pb^{2+} sorption by ion-exchange resins 2–10

An aqueous $(PbNO_3)_2$ solution was prepared such that the molar ratio of the metal ion to calixarene units in the resin packing was 1:1. The $Pb(NO_3)_2$ was dissolved in 0.50 L of DI water. A column containing 1.00 g of resin was washed with 25 mL of 0.010 M HNO_3 and then with 100 mL of DI water at a flow rate of 3.0 mL/min. Of the 0.50-L sample solution, a 2.0-mL portion was removed for Pb^{2+} analysis and a 5.0-mL portion for pH determination. The remainder of the sample solution was passed through the column. A 2.0-mL portion of the effluent was collected for Pb^{2+} analysis. The column was then washed with 100 mL of DI water to remove any unbound metal ions from the packing. The sorbed metal ions were then stripped with 0.010 M HNO_3 at a flow rate of 0.3 mL/min. The Pb^{2+} concentration of the eluant solution, sample solution, and loading effluent was determined by atomic absorption spectrophotometry after appropriate dilution with DI water.

Acknowledgements

This research was supported by Project 003644-0263-2003 from the Technology Development and Transfer Program of the Texas Higher Education Coordinating Board and Grant DE-FG02-90ER14416 from the Division of Chemical Sciences, Geosciences, and Biosciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. We thank the National Science Foundation of Grant CHE-9808436 that was used to purchase the Varian INOVA NMR spectrometer.

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