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Synthesis and Characterization of Calix[4]arene Functionalized Poly(ethylene glycol) Derivatives

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Abstract. Calix[4]arenes with both ligating and methoxy poly(ethylene glycol) groups appended have been synthesized using several approaches, involving the formation of sulfonyl ester groups on the wide rim, Schiff base derivatives on the narrow rim, and thioether groups on both the wide and narrow rims. These new derivatives have been characterized by a combination of infrared and ^{1}H NMR spectroscopy. Compounds **10** and **11** are insoluble in both water and aqueous poly(ethylene glycol), but the other new compounds are soluble.

Key words: calix[4]arene, poly(ethylene glycol)

1. Introduction

Calixarenes are a class of compounds that are useful as phase transfer agents for the extraction of metals from an aqueous into an organic phase [1]. From an environmental viewpoint, it is important to use an organic phase that is inexpensive and non-toxic [2]. As part of our continuing work on poly(ethylene glycol) [3, 4], we have now begun to consider this medium as a potential organic phase. In this paper we describe our approach to synthesizing calix[4]arene functionalized poly(ethylene glycol) oligomers. Both chelate [5–7] and macrocyclic [8, 9] ligands have been functionalized with poly(ethylene glycol). Although other metal complexants have been bound to oligomers, the new compounds described in this paper are among the few examples of calixarenes [10–13] that have both ligating groups and poly(ethylene glycol) functionalities appended to different rims. Such compounds are important because they can be potentially used for biphasic metal separations [14–16].

2. Experimental

2.1. MATERIALS AND METHODS

All materials and solvents were standard reagent grade and were used without further purification unless otherwise noted. Reagents were purchased from Aldrich Chemical Co. and used as supplied. Dry toluene was distilled from

the ketyl prepared from sodium and benzophenone. Dry methylene chloride and chloroform were distilled from calcium hydride. The compound MeO-PEG-OH was either dried under vacuum or by azeotropic distillation from toluene prior to use. ^{1}H NMR spectra were measured using a Bruker AC-200 spectrometer. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer. The compounds 5,11,17,23-tetra(chlorosulfonyl)-25,26,27,28-tetra-(ethoxycarbonylmethoxy)calix[4]arene, and 5,11,17,23-tetra-(chlorosulfonyl)-25, 26, 27, 28-tetra-[(diethylcarbamoyl)methoxy]calix[4]arene, were prepared by a modified literature method [17]. The compounds 5,11,17,23-tetra-*tert*-butyl-25,27-di-(aminoethoxy)-calix[4]arene [18], 5,11,17,23-tetra-[(methylthio)methyl]calix[4]arene [19], 5,11,17,23-tetra-*tert*-butyl 25,26,27,28-tetra-(2-mercaptoethoxy)calix[4]arene [20], MeO-PEG-O_2CCH_2Br [21], and MeO-PEG-NH_2 [22], were prepared according to published procedures.

2.2. SYNTHETIC METHODS

Synthesis of 5,11,17,23-tetra-(chlorosulfonyl)-25,26,27,28-tetra (ethoxycarbonylmethoxy) calix[4]arene **1**

A solution of 25,26,27,28-tetra-(ethoxycarbonylmethoxy)calix[4]arene (1.0 g, 1.3 mmol) in chloroform (20 mL) was treated with chlorosulfonic acid (5 mL) at 0 ° C. The mixture was stirred at 50 °C for 40 min, poured onto ice, and extracted with chloroform (4 × 30 mL). The combined organic phases were washed with water, dried and evaporated to dryness. The crude product was dissolved in chloroform (5 mL) and treated with diethyl ether and hexane. The white precipitate was collected on a glass frit, and washed with diethyl ether. Yield 1.0 g (66%). ^{1}H NMR ($CDCl_3$): δ 1.31 (t, J = 7.0 Hz, 12H, OCH_2CH_3), 3.55 (d, J = 13.8 Hz, 4H, $ArCH_2Ar$), 4.24 (q, J = 7.0 Hz, 8H, OCH_2CH_3), 4.89 (s, 8H, $ArOCH_2$), 5.16 (d, J = 13.8 Hz, 4H, $ArCH_2Ar$), 7.52 (s, 8H, Ar*H*). IR (KBr): ν(C=O) 1752 cm^{-1}. Anal. Calcd. for $C_{44}H_{44}Cl_4O_{20}S_4$: C, 45.5;.H, 3.81. *Found:* C, 45.1; H, 3.83.

Synthesis of 5,11,17,23-tetra-(chlorosulfonyl)-25,26,27,28-tetra-[(diethylcarbamoyl)methoxy]calix[4]arene **2**

A solution of 25,26,27,28-tetra-[(diethylcarbamoyl)methoxy]calix[4]arene (1.3 g, 1.48 mmol) in chloroform (20 mL) was treated with chlorosulfonic acid (6 mL) at 0 °C. The mixture was stirred at 50 °C for 40 min, poured onto ice, and then extracted with chloroform (4 × 30 mL). The combined organic phases were washed with water, dried, and evaporated to dryness. The crude product was dissolved in chloroform (5 mL) and treated with diethyl ether and hexane. The white precipitate was collected on a glass frit and washed with diethyl ether. Yield 1.3 g (69%). ^{1}H NMR ($CDCl_3$): δ 1.16 (m, 24H, NCH_2CH_3), 3.34 (q, J = 7.0 Hz, 16H, NCH_2CH_3), 3.50 (d, J = 13.4 Hz, 4H, $ArCH_2Ar$), 5.18 (s, 8H, $ArOCH_2$), 5.68 (d, J = 13.4 Hz,

4H, ArCH_2Ar), 7.51 (s, 8H, ArH). IR (KBr): ν(C=O) 1654 cm^{-1}. *Anal. Calcd.* for $C_{52}H_{64}Cl_4N_4O_{16}S_4$: C, 49.1; H, 5.07. *Found:* C, 49.0; H, 5.22.

2.2.1. *Synthesis of 25,26,27,28-tetra-[H_2NCH_2CH_2NHC(O)CH_2O]calix[4]arene* **3**

To a cold solution of 25,26,27,28-tetra-(ethoxycarbonylmethoxy)calix[4]arene (0.80 g, 1.04 mmol) in tetrahydrofuran (5 mL) was added ethylenediamine (40 mL, 598 mmol). The mixture was stirred at room temperature for 7 days. The solvent and excess ethylenediamine were then removed under reduced pressure, and the residue was treated with water. The resulting white solid was collected by filtration, washed with water, a mixture of water and methanol, and dried in vacuum. Yield 0.82 g (95%). ^{1}H NMR ($CDCl_3$): δ 1.72 (s, 8H, NH_2), 2.83 (m, 8H, CH_2N), 3.15–3.50 (m, 12H, ArCH_2Ar and CH_2N), 4.48 (s, 8H, CH_2O), 4.10–4.70 (m, 4H, ArCH_2Ar), 6.50–6.80 (m, 12H, ArH), 7.45, 7.91 (t, t, 4H, NH). IR (KBr): ν(CO) 1654 cm^{-1}. *Anal. Calcd.* for $C_{44}H_{56}N_8O_{8.}3CH_3OH$: C, 61.3; H, 7.44; N, 12.2. *Found* C, 62.0; H, 6.75; N, 11.7.

Synthesis of p-(MeO-PEG-O_2CCH_2O)-C_6H_4CHO **4**

A mixture of *p*-HOC_6H_4CHO (230 mg, 1.9 mmol), K_2CO_3 (260 mg, 1.9 mmol) and MeO-PEG-O_2CCH_2Br (4 g, 1.9 mmol) in acetonitrile (50 mL) was refluxed for 3 days. The suspension was then cooled and filtered, and the filtrate evaporated. The residue was treated with hydrochloric acid (50 mL of 0.5 M), and extracted with chloroform (3 × 50 mL). The combined organic phases were washed with water (2 × 50 mL), dried, and evaporated to dryness. The residue was dissolved in methylene chloride (10 mL), and treated with diethyl ether at 0 °C. The white precipitate was collected on a glass frit, and washed with diethyl ether. Yield 3.0 g (73%). ^{1}H NMR ($CDCl_3$): δ 3.38 (s, OCH_3), 3.40–4.05 (m, (OCH_2CH_2)$_n$), 4.38 (t, CO_2CH_2), 4.77 (s, ArOCH_2), 7.03 (d, ArH). 7.79 (d, ArH), 9.91 (s, ArCOH). IR (KBr): ν(CH_2OCH_2) 1117 cm^{-1}, ν(C=O) 1684 1757 cm^{-1}.

2.2.2. *Synthesis of 5,11,17,23-tetra-(MeO-PEG-OSO_2)-25,26,27,28-tetra-(ethoxycarbonyl methoxy)calix[4]arene* **5**

To a cold solution of MeO-PEG-OH (M = 2000, 1.04 g, 0.52 mmol) in dry toluene (15 mL), was added sodium hydride (50 mg, 2.08 mmol). The mixture was stirred at room temperature for 3 h, then at 50 °C for 1 h. The mixture was filtered, cooled to 0 °C, and **1** (150 mg, 0.13 mmol) was added. The solution was stirred for 48 h at room temperature, filtered, and treated with diethyl ether (200 mL). The crude product was collected on a glass frit, and reprecipitated twice from methylene chloride with diethyl ether, and dried in vacuum. Yield 0.9 g (77%). ^{1}H NMR ($CDCl_3$): δ 1.31 (m, OCH_2CH_3), 3.38 (s, OCH_3), 3.20–4.10 (m, (OCH_2CH_2)$_n$, ArCH_2Ar), 4.22 (q, OCH_2CH$_3$), 4.85 (s, ArOCH_2), 5.10 (d, ArCH_2Ar), 7.32 (s, ArH). IR (KBr): ν(CH_2OCH_2) 1115 cm^{-1}, ν(C=O) 1752 cm^{-1}.

Synthesis of 5,11,17,23-tetra-(MeO-PEG-OSO$_2$)-25,26,27,28-tetra-[(diethyl-carbamoyl)methoxy)calix[4]arene **6**

To a cold solution of MEO-PEG-OH (M = 2000, 1.04 g, 0.52 mmol) in dry toluene (15 mL) was added sodium hydride (50 mg, 2.08 mmol). The mixture was stirred at room temperature for 3 h, then at 50 °C for 1 h. The mixture was filtered, cooled to 0 °C, and **2** (165 mg, 0.13 mmol) was added. The solution was stirred for 48 h at room temperature, filtered, and treated with diethyl ether (200 mL). The crude product was collected on a glass frit, reprecipitated twice from methylene chloride with diethyl ether, and dried in vacuum. Yield 0.8 g (67%). ^{1}H NMR ($CDCl_3$): δ 1.16 (m, NCH_2CH_3), 3.38 (s, OCH_3), 3.45–4.10 (m, $(OCH_2CH_2)_n$, $ArCH_2Ar$, NCH_2CH_3), 5.13 (s, $ArOCH_2$), 5.61 (d, $ArCH_2Ar$), 7.34 (s, Ar*H*). IR (KBr): $\nu(CH_2OCH_2)$ 1115 cm^{-1}, ν(C=O) 1654 cm^{-1}.

Synthesis of 5,11,17,23-tetra-(MeO-PEG NHSO$_2$)-25,26,27,28-tetra (ethoxycarbonyl methoxy)calix[4]arene **7**

A mixture of MeO-PEG-NH_2 (M = 2000, 1.0 g, 0.5 mmol) and triethylamine (1 ml) in dry methylene chloride (5 mL) was mixed with a solution of **1** (145 mg, 0.125 mmol) dissolved in dry methylene chloride (10 mL) at 0 °C. The mixture was stirred at room temperature for 24 h, then evaporated to dryness. The residue was dissolved in hydrochloric acid (50 mL of 0.5 M), and the solution extracted with chloroform (4 × 50 mL). The combined organic phases were washed with water (2 × 50 mL), dried, and evaporated to dryness. The residue was dissolved in methylene chloride (10 mL) and treated with diethyl ether at 0 °C. The white precipitate was collected on a glass frit and washed with diethyl ether. Yield 0.5 g (44%). ^{1}H NMR ($CDCl_3$): δ 1.31 (t, OCH_2CH_3), 2.98 (m, NCH_2), 3.38 (s, OCH_3), 3.42–4.15 (m, $(OCH_2CH_2)_n$, $ArCH_2Ar$), 4.26 (q, OCH_2CH_3), 4.82 (s, $ArOCH_2$), 5.02 (d, $ArCH_2Ar$), 5.72 (t, SO_2NH), 7.32 (s, Ar*H*). IR(KBr): $\nu(CH_2OCH_2)$ 1112 cm^{-1}, ν(C=O) 1756 cm^{-1}.

Synthesis of 5,11,17,23-tetra-(MeO-PEG-NHSO$_2$)-25,26,27,28-tetra[(diethyl-carbamoyl)methoxy] calix[4]arene **8**

A mixture of MeO-PEG-NH_2 (M = 2000, 1.0 g, 0.5 mmol) and triethylamine (1 mL) in dry methylene chloride (5 mL) was mixed with a solution of **2** (160 mg, 0.125 mmol) dissolved in dry methylene chloride (10 mL) at 0 °C. The mixture was stirred at room temperature for 24 h, then evaporated to dryness. The residue was dissolved in hydrochloric acid (50 mL of 0.5 M), and the solution extracted with chloroform (4 × 50 mL). The combined organic phases were washed with water (2 × 50 mL), and evaporated to dryness. The residue was dissolved in methylene chloride (10 mL) and treated with diethyl ether at 0 °C. The white precipitate was collected on a glass frit, and washed with diethyl ether. Yield 0.6 g (53%). ^{1}H NMR ($CDCl_3$): δ 1.14 (m, NCH_2CH_3), 2.94 (m, NCH_2), 3.38 (s, OCH_3), 3.40–4.20

(m, (OCH_2CH_2)$_n$, ArCH_2Ar, NCH$_2$CH_3), 5.01 (s, ArOCH_2), 5.53 (m, ArCH_2Ar, SO$_2$NH), 7.38 (s, ArH). IR(KBr): ν(CH$_2$OCH$_2$) 1113 cm^{-1}, ν(C=O) 1655 cm^{-1}.

Synthesis of 25,26,27,28-tetra-[p-(MeO-PEG-O$_2$CCH$_2$O)C$_6$H$_4$CHNCH$_2$CH$_2$-NHC(O)CH$_2$]calix[4]arene **9**

A mixture of **3** (83 mg, 0.10 mmol), **4** (0.86 g, 0.4 mmol) and sulfuric acid (1 mL of 0.2 M) in methanol (15 mL) was refluxed for 5 h. After filtration, the filtrate was treated with diethyl ether at 0 °C. The resulting white precipitate was collected on a glass frit, and washed with diethyl ether. The crude product was reprecipitated twice from methylene chloride with diethyl ether, and dried in vacuum. Yield 0.6 g (64%). ^{1}H NMR (CD$_3$OD): δ 3.06–4.02 (m, OCH_3, (OCH_2CH_2)$_n$, ArCH_2Ar, CH_2N), 4.20–5.05 (m, CO$_2$CH_2, ArCH_2Ar, ArOCH_2), 6.59 (s, ArH, NH), 6.88 (d, ArH), 7.0 (d, ArH), 8.50 (s, CH=N). IR(KBr): ν(CH$_2$OCH$_2$) 1115 cm^{-1}, ν(C=O) 1654, 1752 cm^{-1}, ν(C=N) 1640 cm^{-1}.

Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-di[p-(MeO-PEG-O$_2$CCH$_2$O)-C$_6$H$_4$CHNCH$_2$CH$_2$O]calix[4]arene **10**

A mixture of 5,11,17,23-tetra-*tert*-butyl-25,27-di(aminoethoxy)calix[4] arene (134 mg, 0.18 mmol), **4** (0.80 g, 0.36 mmol) and sulfuric acid (1 mL of 0.2 M) in ethanol (15 mL) was refluxed for 7 h. After filtration, the filtrate was treated with diethyl ether at 0 °C. The resulting white precipitate was collected on a glass frit, and washed with diethyl ether. The crude product was reprecipitated twice from methylene chloride with diethyl ether, and dried in vacuum. Yield 0.66 g (73%). ^{1}H NMR (CDCl$_3$): δ 0.95 (s, C(CH_3)$_3$), 1.28 (s, C(CH_3)$_3$), 3.38 (s, OCH_3), 3.10–4.16 (m, (OCH_2CH_2)$_n$, ArCH_2Ar, ArOCH_2, NCH_2), 4.31 (d, ArCH_2Ar), 5.05 (s, ArOCH_2CO$_2$), 6.76 (s, ArOH), 7.00 (d, ArH), 7.12 (s, ArH), 7.33 (s, ArH), 7.75 (d, ArH), 8.41 (s, CH=N). IR (KBr): ν(CH$_2$OCH$_2$) 1109 cm^{-1}, ν(C=O) 1762 cm^{-1}, ν(C=N) 1648 cm^{-1}.

Synthesis of 5,11,17,23-tetra-[(methylthio)methyl]-25,27-(MeO-PEG-O$_2$CCH$_2$O)calix[4]arene **11**

A mixture of 5,11,17,23-tetra-[(methylthio)methyl)calix[4]arene (156 mg, 0.23 mmol), K$_2$CO$_3$ (200 mg, 1.4 mmol) and MeO-PEG-O$_2$CCH$_2$Br (1 g, 0.47 mmol) in acetone (50 mL) was refluxed for 5 days. The suspension was then cooled, filtered, and the filtrate was evaporated to dryness. The residue was treated with hydrochloric acid (50 mL of 0.5 M), and extracted with chloroform (3 × 60 mL). The combined organic phases were washed with water (2 × 50 mL), and evaporated to dryness. The residue was dissolved in methylene chloride (10 mL), and treated with diethyl ether at 0 °C. The white precipitate was collected on a glass frit and washed with diethyl ether. Yield 0.7 g (64%). ^{1}H NMR (CDCl$_3$): δ 1.96 (s, SCH_3), 2.18 (s, SCH_3), 3.38 (s, OCH_3), 3.20–4.02 (m, (OCH_2CH_2)$_n$, ArCH_2Ar, SCH_2),

4.28 (m, CO_2CH_2, $ArCH_2Ar$), 4.70 (s, $ArOCH_2$), 7.03 (s, ArH), 10.15 (s, $ArOH$). IR (KBr): $\nu(CH_2OCH_2)$ 1111 cm^{-1}, ν(C=O) 1735 cm^{-1}.

Synthesis of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetra-(MeO-PEG-$O_2CCH_2SCH_2CH_2O$)calix[4]arene **12**

To a cold solution of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetra-(2-mercapto-ethoxy)calix[4]arene (105 mg, 0.118 mmol) and MeO-PEG-O_2CCH_2Br (1 g, 0.47 mmol) in tetrahydrofuran (15 mL) was added triethylamine (0.1 mL, 0.72 mmol). The mixture was stirred at room temperature for 30 h, then at 50 °C for 3 h, followed by evaporation to dryness. The residue was dissolved in hydrochloric acid (50 mL of 0.1 M), and the solution extracted with chloroform (4 × 50 mL). The combined organic phases were washed with water (2 × 50 mL), dried, and evaporated to dryness. The residue was dissolved in methylene chloride (10 mL), and treated with diethyl ether at 0 °C. The white precipitate was collected on a glass frit and washed with diethyl ether. Yield 0.8 g (74%). ^{1}H NMR ($CDCl_3$): δ 1.01 (s, $C(CH_3)_3$), 3.15 (m, $ArCH_2Ar$, SCH_2), 3.38 (s, OCH_3), 3.57 (m, $(OCH_2CH_2)_n$), 3.97 (m, $ArOCH_2$), 4.25 (m, $ArCH_2Ar$, CO_2CH_2), 4.62 (s, SCH_2CO_2), 6.70 (s, ArH). IR (KBr): $\nu(CH_2OCH_2)$ 1116 cm^{-1}, ν(C=O) 1736 cm^{-1}.

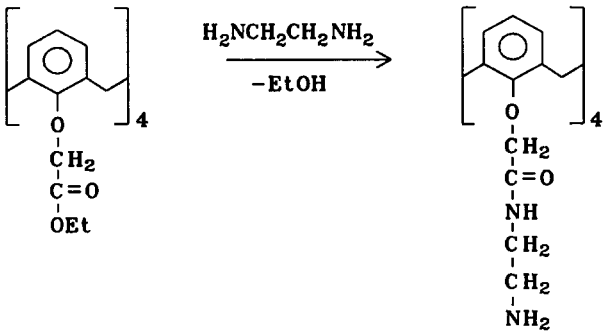
3. Results and Discussion

An important development in calixarene chemistry is the recognition that by the judicious choice of substituents, these compounds can be selective complexants for metal ions [23]. Among the functionalities that have been used in this capacity are those having oxygen, nitrogen or sulfur donor groups [18–20]. In developing these compounds as selective extractants for metal ions from an aqueous into an organic phase, the choice of the organic liquid phase is important. In many cases chloroform or methylene chloride are used, but these liquids present too many environmental problems to be employable on a large scale. Hydrocarbons are an alternative to these chlorocarbons, but they can also be toxic as well as being flammable.

Another approach is to use the non-toxic, non-flammable, biphasic and hydrophilic ether poly(ethylene glycol) as extractant. This compound has the additional advantage that it can be potentially used for the simultaneous extraction of both metals and organics that are commonly present in soils and waters. A limitation to this approach, however, is that since calixarenes often have low solubility in both water and ethers, they cannot be used as phase transfer extractants in these media. In order to circumvent this limitation, we have now functionalized a series of calix[4]arenes with oxyethylene groups in order to make them more compatible with both water and poly(ethylene glycol). The chosen calix[4]arenes are ones having oxygen, nitrogen and sulfur groups that can function as donor ligands to selected metal ions, and routes to put methoxy poly(ethylene glycol) groups on

either the upper or lower rim have been used. ^{1}H NMR spectroscopy reveals that all these new compounds are in the cone conformation.

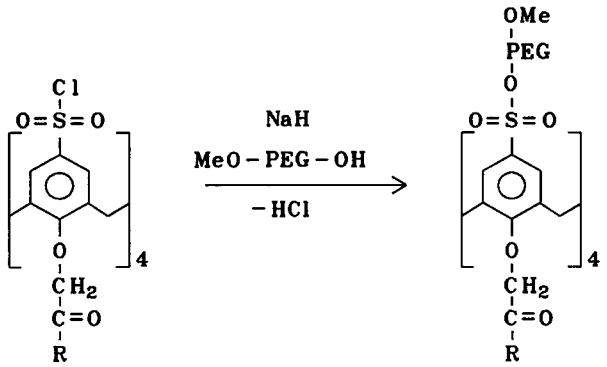
Compounds **1** and **2** with chlorosulfonyl groups on the wide rim have been prepared by standard routes. Compound **3** with a substituted ethylenediamine functionality on the narrow rim has been prepared by reacting 25,26,27,28-tetra(ethoxycarbonylmethoxy)calix[4]arene with ethylenediamine (Equation 1).



(1)

3

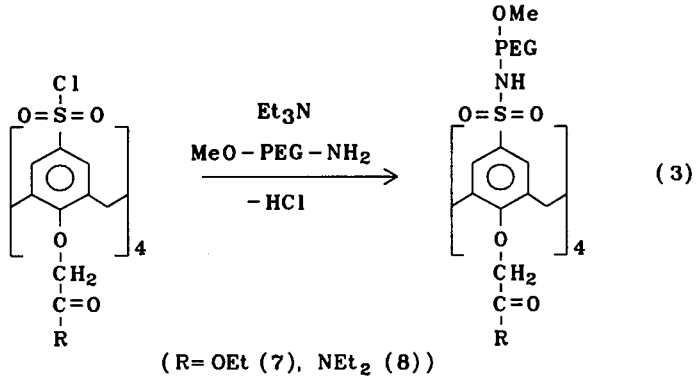
Several approaches have been used to attach oxyethylene groups onto the calix[4]arene host. One of these approaches involves using calix[4]arenes with chlorosulfonyl moeities on the wide rim, and then reacting them with MeO-PEG-OH (Equation 2).



(2)

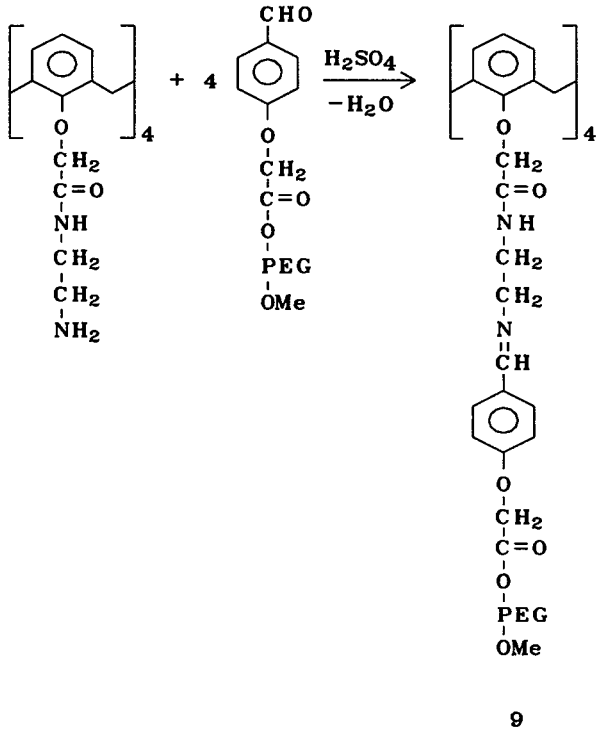
(R= OEt(5), NEt_2(6))

An analogous approach involves reacting the chlorosulfonyl substituted calix[4]arene with MeO-PEG-NH_2 (Equation 3).



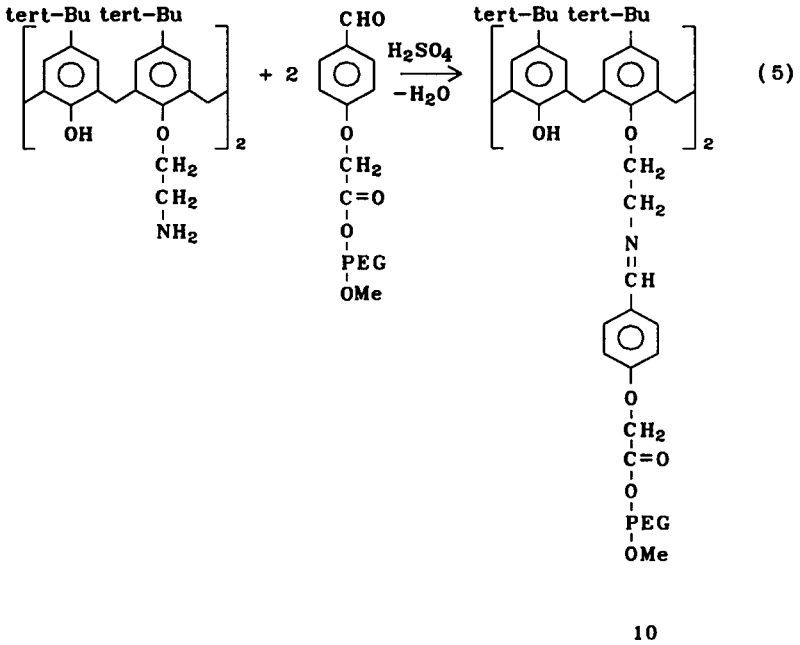
(3)

A different approach that we have used involves carrying out a Schiff base reaction with an aldehyde to which an oxyethylene group has been appended. This latter route allows the oxyethylene substituent to be attached to the narrow rim of the calix[4]arene. This approach has been used to substitute either all four (Equation 4),



(4)

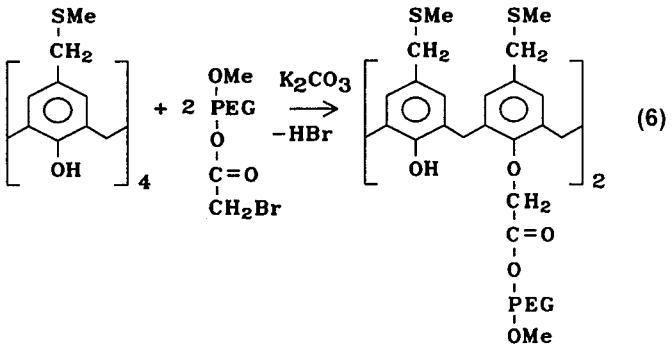
or just two, (Equation 5)



(5)

10

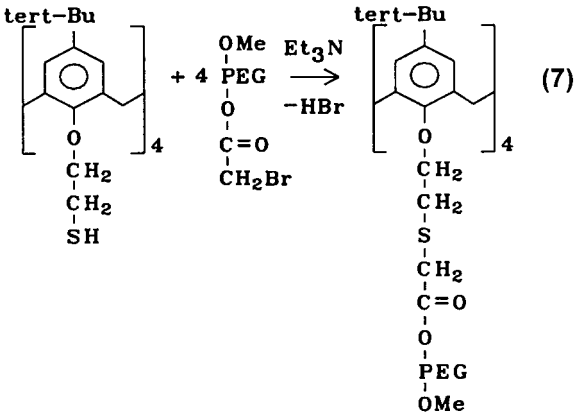
of the narrow rim positions. Yet another route to attaching oxyethylene groups to calix[4]arenes involves an alkylation strategy. This approach has been used to prepare oxyethylene derivatized calixarenes that have thioether moeities attached to either the wide (Equation 6)



(6)

11

or the narrow (Equation 7) rims.



(7)

12

All of these new compounds and their poly(ethylene glycol) derivatives show the expected ^{1}H NMR peaks for the aromatic (ArH), bridging methylene ($ArCH_2Ar$), and alkoxy (OCH_2) groups of the calix[4]arene skeleton. In addition, the ^{1}H NMR spectra confirm the presence of the individual substituent groups on the different derivatized calix[4]areres. For the amide derivatives, the presence of a carbonyl group is confirmed by the presence of a carbonyl stretch band in the 1650–1750 cm^{-1} region. For the calix[4]arenes bound to the poly(ethylene glycol) derivatives there are additional resonances in the ^{1}H NMR spectra in the δ 3.00–4.30 range for the $(OCH_2CH_2)_n$ groups.

The solubility properties of these poly(ethylene glycol) functionalized calix[4]arenes, with the exception of compounds **10** and **11**, match those expected for such derivatives, and are soluble in both water and aqueous poly(ethylene glycol). These compounds with metal binding sites, and deep well cavities created by the poly(ethylene glycol) substituents, have potentially useful applications as host molecules.

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References

1. A. T. Yordanov and D. M. Roundhill: *Coord. Chem. Revs.* **170**, 93 (1998).
2. J. M. Harris (ed.): *Poly(ethylene Glycol) Chemistry: Biotechnical and Biomedical Applications*, Plenum, New York (1992).
3. R. Tzevi, P. Novakov, K. Troev, and D. M. Roundhill: *J. Polym. Sci.: Part A: Polym. Chem.* **35**, 625(1997).

4. R. Tzevi, G. Todorova, K. Kossev, K. Troev, E. M. Georgiev, and D. M. Roundhill: *Makromol. Chem.* **194**, 3261 (1993).
5. P. A. Aguinaga-Diaz and R. Z. Guzman: *Sep. Sci. Technol.* **31**, 1483 (1996).
6. A. D. Pozzo, A. Vigo, and G. Donzelli: *Makromol. Chem.* **190**, 2457 (1989).
7. M. Leonard and E. Dellacherie: *Makromol. Chem.* **189**, 1809 (1988).
8. J. M. Harris, N. H. Hundley, T. G. Shannon, and E. C. Struck: *J. Org. Chem.* **47**, 4789 (1982).
9. J. W. Long II, K. Kim, and R. W. Murray: *J. Am. Chem. Soc.* **119**, 11510 (1997).
10. J. W. Cornforth, E. D. Morgan, K. T. Potts, and R. J. W. Rees; *Tetrahedron* **29**, 1659 (1973).
11. Y. Shi and Z. Zhang: *J. Chem. Soc., Chem. Com.*, 375 (1994).
12. K. Araki, A. Yanagi, and S. Shinkai: *Tetrahedron* **49**, 6763 (1993).
13. E. Nomura, H. Taniguchi, K. Kawaguchi, and Y. Otsuji: *J. Org. Chem.* **58**, 4709 (1993).
14. R. D. Rogers, A. H. Bond, C. B. Bauer, J. Zhang, M. L. Jezl, D. M. Roden, S. D. Rein, and R. R. Chomko: *Aqueous Biphasic Separations: Biomolecules to Metal Ions*, R. D. Rogers and M. A. Eiteman (eds.), Plenum, New York (1995), pp. 1–20.
15. R. D. Rogers and J. Zhang: *Ion Exchange and Solvent Extraction*, J. A. Marinsky and Y. Marcus (eds.), Marcel Dekker, New York, 1997, Vol.13, Ch. 4, pp. 141–193.
16. R. D. Rogers, A. H. Bond, and C. B. Bauer: *Sep. Sci. Technol.* **28**, 1091 (1993).
17. Y. Morzherin, D. M. Rudkevich, W. Verboom, and D. N. Reinhoudt: *J. Org. Chem.* **58**, 7602 (1993).
18. E. M. Georgiev, N. Wolf, and D. M. Roundhill: *Polyhedron* **16**, 1581 (1997).
19. A. T. Yordanov, O. M. Falana, H. F. Koch, and D. M. Roundhill: *Inorg. Chem.* **36**, 6468 (1997).
20. A. T. Yordanov, J. T. Mague, and D. M. Roundhill: *Inorg. Chem.* **34**, 5084 (1995).
21. H. Han and K. D. Janda: *J. Am. Chem. Soc.* **118**, 2540 (1996).
22. R. Greenwald, A. Pendri, and D. Bolikal: *J. Org. Chem.* **60**, 331 (1995).
23. D. M. Roundhill: *Progr. Inorg. Chem.* **43**, 533 (1995).