

Calixarenes enhanced as dendrimers: association of 1,3-alternate calix[4]crowns with cone calix[4]arenes structures

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ABSTRACT

It is reported the synthesis of multicalixarenes **3** and **5-9** combining calix[4]crowns in the 1,3-alternate conformation and parent calix[4]arenes in the cone conformation.

Key words : Calixarenes, cesium removal, dendrimers

Introduction

Calixarenes (1) have been exploited in all areas of supramolecular chemistry (2) over the past four decades and many recent developments have concerned their applications in the production of chemical entities with the dimensions of nanometres as in 'nanochemistry' (3). One of the most important use of calixarenes is the treatment of nuclear wastes (4). The use of calixcrowns-6 compounds in the 1,3- alternate conformation for the removal of radioactive cesium from waste waters to dispose of wastes in environmentally acceptable ways that minimise the volume of both low- and high-activity materials has been recently highlighted (5). With the event of nanochemistry, and consequent research on such molecular materials,⁶ related works have been published involving calixcrowns in nanostructures. For example Bu *et al* (7), reported the convergent-synthesis of the second generation of a dendrimer based on calixcrown in the 1,3-alternate conformation with obvious potential uses in cesium removal

from nuclear waste waters. In a series of papers, Jankowski, Mauclaire *et al.* (8), prepared several 1,3-calixbiscrown-cyclo-dextrin coupling products for their use as tubular phases and complexants for nanofiltration as well. These articles prompted us to publish some of our recent findings in the same areas of research.

In this communication we report the synthesis of calixcrowns ligands **5-9** which are large multi-calixarenes some of them with dendrimer structures prepared for materials for cesium removal. All of them contain the 1,3-calix[4] crown-6 moiety which is known to be highly Cs/a-selective (5). According to a synthetic work⁹ published by us to prepare calix-dendrimers (10), the synthesis of tricalix **3** was performed by reacting diamino 1,3-calix[4]monobenzocrown **6** (**1**) (11) with 2 equiv. of mono methyl ester calix[4]arene (**2**) (9a), (9b) in a minimum of 1:1 methanol:toluene mixture (see **Fig 1**). After 7 days of reflux under nitrogen and complete evaporation of solvents, the residue was chromatographed on silica column (9:1 CH₂Cl₂:acetone as eluent). **3** was obtained pure as white powder in 38% yield. Mass spectrometry MALDI-TOF showed that the derivative **3** is $m/z = 2297.4$ (C₁₄₈H₁₇₈N₂O₁₈ + Na⁺).

Fig 2 shows the synthesis of dendrimeric structures **5-9**. 4-Days-reflux of a mixture of diamino 1,3-calix[4] bisbenzocrown-6 (**4**) (11) and 4 equiv of **2** in a minimum of 1:1 meth-

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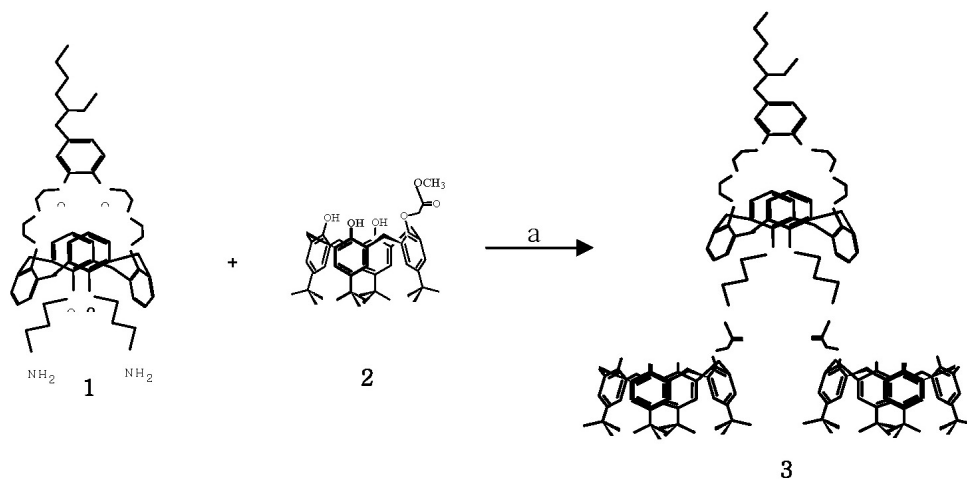


Fig 1. Synthesis of tricalix 3.(a) 2, 1:1 methanol:toluene, 7d-reflux.

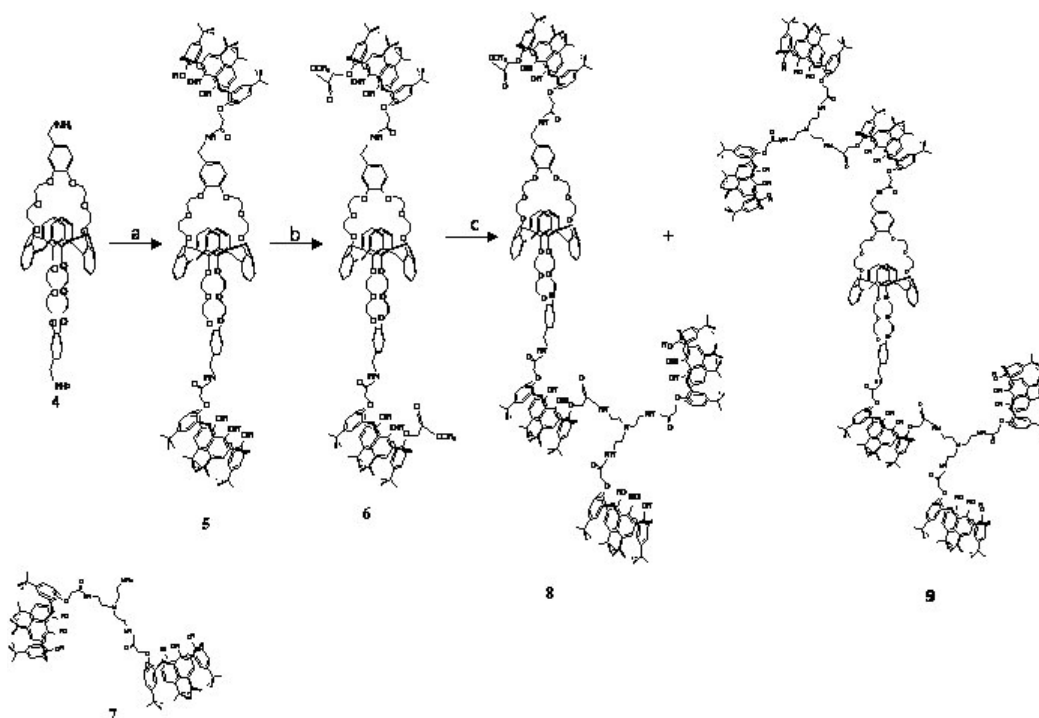


Fig 2. Synthesis of 5-9.(a) 2, 1:1 methanol:toluene, 4d-reflux. (b) $\text{BrCH}_2\text{CO}_2\text{Me}$, K_2CO_3 , acetonitrile, 1d-reflux.(c) 7, 1:1 methanol:toluene, 4d-reflux.

anol:toluene, followed by a treatment similar to **1**, gave tricalix **5** as a white solid in 18 % yield. The double addition was deduced from the MALDI-TOF showing a peak at $m/z = 2399.23$ ($5 + \text{K}^+$). According to reference (9a) **5** was selectively di-alkylated into dimethyl ester tricalix **6**, by reaction with 3 equiv of $\text{BrCH}_2\text{CO}_2\text{Me}$ and an excess of K_2CO_3 in refluxing acetonitrile for 1 day. After acidic work-up, **6**

was obtained pure by columning on silica with a mixture 9:1 CH_2Cl_2 :acetone as eluent. The yield was 54 %. Mass spectrometry MALDI-TOF displayed a peak at $m/z = 2544.28$ ($6 + \text{K}^+$). Dimethyl ester tricalix **6** was condensed with trendicalix **7** (9a), (9f) (in similar conditions as the preparation of **3** and **5**) to give pentacalix **8** in 7 % yield. Mass spectrometry MALDI-TOF gave a peak at $m/z = 3998.5$. Heptacalix

9 has only been detected by running mass spectrometry (m/z = 5109.2) on residual crops of column chromatography but could not be purified.

The analytical data were in agreement with the molecular structures of multi calix[4]arenes **3** and **5-8**. The ArCH_2Ar protons of the original 1,3-alternate calix[4]crown-6 was maintained and detected as a singlet while the ArCH_2Ar protons of the cone calix[4]arenes were observed as characteristic AB and A'B' systems in the (1) H NMR spectra of **3** and **5-8 (9)**. The formation of the amido function was deduced from the presence of a triplet corresponding to the CONH protons (**9**).

To conclude, in the present paper we report the synthesis of five new multi-calixarenes **3** and **5-8** which can be seen as new dendrimeric structures based on calixarenes. Future work is directed towards the involvement of these structures as recovering agents of cesium in nanofiltration techniques and as grafted dendrimers on polymers.

Experimental section

Preparation of 3:1 (11) (103 mg, 0.114 mmol), **2** (180 mg, 0.249 mmol), 1:1 methanol:toluene (2 ml) were refluxed for 7d. After evaporation under reduced pressure, the residue was dissolved in a minimum of CH_2Cl_2 . Chromatography on a SiO_2 column (9:1 CH_2Cl_2 /acetone) gave pure **3**. White solid. Mp 185-187 °C. (1) H NMR (CDCl_3):10.22 (s large, 1H, ArOH), 10.18 (s, 1H, ArOH), 9.52 (s large, 2H, ArOH), 9.46 (s, 2H, ArOH), 9.00 (t, 1H, J = 5.4 Hz, NH amide), 8.91 (t, 1H, J = 4.8 Hz, NH amide), 7.14-6.97 (m, 16H, ArH), 6.93-6.59 (m, 15H, ArH), 4.64 (s, 2H, OCH_2CO), 4.51 (s, 2H, OCH_2CO), 4.39-3.99 (m, 22H, CH_2CH_2 , ArCH_2Ar), 3.97-3.63 (m, 23H, CH_2CH_2 , ArCH_2Ar), 3.62-3.14 (m, 18H, CH_2CH_2 , CH_2CH), 1.95-1.82 (m, 6H, CH_3), 1.27 (s, 18H, *tert*-butyl), 1.24 (s, 18H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl), 1.20 (s, 9H, *tert*-butyl), 1.19 (s, 9H, *tert*-butyl). MW = 2273.04 calculated for $\text{C}_{148}\text{H}_{178}\text{N}_2\text{O}_{18}$, (MALDI-TOF) m/z = 2297.4 ($3 + \text{Na}^+$). Yield 38 %.

Preparation of 5:4 (11) (40 mg, 0.04 mmol), **2** (117 mg, 0.162 mmol), 1:1 methanol:toluene (2 ml) were refluxed for 4d. After evaporation under reduced pressure, the residue was dissolved in a minimum of CH_2Cl_2 . Chromatography on a

SiO_2 column (9:1 CH_2Cl_2 /acetone) gave pure **5**. White solid. Mp 217-219 °C. (1) H NMR (CDCl_3):9.92 (s, 2H, ArOH), 9.66 (t, 2H, J = 5.4 Hz, NH amide), 9.33 (s, 4H, ArOH), 7.20-7.00 (m, 30H, ArH), 6.64 (t, J = 7.5 Hz, 4H, ArH), 4.66 (d, 4H, J = 6.0 Hz, NHCH_2), 4.60 (s, 4H, OCH_2CO), 4.15 (d, 8H, J = 13.5 Hz, AB system, A'B' system, ArCH_2Ar), 4.08 (q, 8H, J = 4.5 Hz, ArCH_2Ar), 3.72-3.49 (m, 32H, CH_2CH_2), 3.45 (d, 8H, J = 13.5 Hz, AB system, A'B' system, ArCH_2Ar), 1.22 (s, 36H, *tert*-butyl), 1.21 (s, 18H, *tert*-butyl), 1.19 (s, 18H, *tert*-butyl). MW = 2361.06 calculated for $\text{C}_{150}\text{H}_{178}\text{N}_2\text{O}_{22}$, (MALDI-TOF) m/z = 2399.23 ($5 + \text{K}^+$). Yield 18 %.

Preparation of 6:5 (30 mg, 0.012 mmol), K_2CO_3 (2 mg, 19×10^{-4} mmol), $\text{BrCH}_2\text{CO}_2\text{CH}_3$ (6 mg, 0.038 mmol) and acetonitrile (2 ml) were refluxed for 1d. After evaporation under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with aqueous 1N HCl. The organic layer was dried over Na_2SO_4 , filtered and evaporated. Chromatography on a SiO_2 column (9:1 CH_2Cl_2 :acetone as eluent) gave pure **6**. White solid. Mp 212-214 °C. (1) H NMR (CDCl_3):9.24 (t, 2H, J = 6.0 Hz, NH amide), 7.56 (s, 4H, ArOH), 7.16-6.87 (m, 30H, ArH), 6.68 (t, 4H, J = 7.5 Hz, ArH), 4.74 (d, 4H, J = 6.2 Hz, NHCH_2), 4.61 (s, 4H, OCH_2CO), 4.54 (s, 4H, OCH_2CO), 4.31 (d, 4H, J = 13.20 Hz, AB system, ArCH_2Ar), 4.15 (d, 4H, J = 12.99 Hz, A'B' system, ArCH_2Ar), 4.05 (t, 8H, J = 4.8 Hz, CH_2CH_2), 3.86 (m, 8H, CH_2CH_2), 3.67 (s, 6H, OCH_3), 3.56-3.35 (m, 32H, CH_2CH_2 , AB system, A'B' system, ArCH_2Ar), 1.29 (s, 36H, *tert*-butyl), 1.00 (s, 18H, *tert*-butyl), 0.99 (s, 18H, *tert*-butyl). MW= 2505.19 calculated for $\text{C}_{156}\text{H}_{186}\text{N}_2\text{O}_{26}$, (MALDI-TOF) m/z = 2544.28 ($6 + \text{K}^+$). Yield 54 %.

Preparation of 8:6 (20 mg, 0.008 mmol), **7** (48 mg, 0.032 mmol), 1:1 methanol:toluene (2 ml) were refluxed for 28d. After evaporation under reduced pressure, the residue was dissolved in a minimum of CH_2Cl_2 . Chromatography on a SiO_2 column (8:2 CH_2Cl_2 /acetone) gave pure **8**. White solid. Mp 195-197 °C. (1) H NMR (CDCl_3) : 9.36 (t, 2H, J = 2.1 Hz, NH amide), 9.30 (t, 1H, J = 2.4 Hz, NH amide), 9.25 (t, 1H, J = 6.0 Hz, NH amide), 9.10 (t, 1H, J = 4.5 Hz, NH amide), 7.94 (s, 2H, ArOH), 7.61 (s, 4H, ArOH), 7.57 (s, 4H, ArOH), 7.06 (s, 16H, ArH), 7.03 (d, 16H, J = 3.9 Hz, ArH), 6.95 (d, 4H, J = 2.4 Hz, ArH), 6.91 (s, 4H, ArH), 6.87 (d, 6H, J = 2.4 Hz, ArH), 6.67 (t, 4H, J = 9.0 Hz, ArH), 4.73 (d, 4H, J = 5.7 Hz, NHCH_2Ar), 4.60 (s, 8H, OCH_2CO), 4.53 (s, 4H, OCH_2CO),

4.34-3.85 (m, 44H, CH₂CH₂, AB system, A'B'system, ArCH₂Ar), 3.76 (t, 8H, *J* = 5.1 Hz, CH₂CH₂), 3.72 (s, 8H, CH₂CH₂), 3.67 (s, 3H, OCH₃), 3.63-3.31 (m, 24H, CH₂CH₂, AB system, A'B'system, ArCH₂Ar), 1.28 (s, 18H, *tert*-butyl), 1.26 (d, 18H, *J* = 9.0 Hz, *tert*-butyl), 1.22 (s, 9H, *tert*-butyl), 1.21 (s, 9H, *tert*-butyl), 1.20 (s, 72H, *tert*-butyl), 1.16 (s, 9H, *tert*-butyl). MW = 3997.27 calculated for C₂₅₃H₃₁₂N₆O₃₅, (MALDI-TOF) *m/z* = 3998.5. Yield 7 %.

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