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Trianionic calix[4]arene monoalkoxy derivatives: synthesis, solid-state structures and self-assembly properties†

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The synthesis of a series of novel tris[(carboxy)methyl]-monoalkoxy-trihydroxycalix[4]arenes is described. Treatment of the tris[(dimethylamino)methyl]-monoalkoxy-trihydroxycalix[4]arene derivatives with iodomethane, followed by sodium cyanide as a nucleophile, gave the corresponding tris[(cyano)methyl]-monoalkoxy-trihydroxycalix[4]arenes in excellent yield, and these latter compounds were converted by hydrolysis to their tris[(carboxy)methyl]-monoalkoxy derivatives. The solid-state structures of four of the intermediate tris[(cyano)methyl]-monoalkoxy-trihydroxycalix[4]arenes show inclusion of an acetonitrile guest in the ethoxy derivative and intermolecular inclusion of the hydrophobic terminal region of the alkoxy groups for longer chain lengths. The packing of both structural types show 1-D inclusion polymer behaviour. At pH values above 5.5, all the trianionic tris[(carboxy)methyl]-monoalkoxy-trihydroxycalix[4]arene derivatives showed self-assembly to yield micellar systems, for which there was a clear odd–even effect in the observed surface tensions at the critical micelle concentrations.

Introduction

The design and construction of amphiphilic supramolecular platforms[1,2] is of interest for the transport of bioactive molecules, such as liposomes,[3] nanospheres[4] or solid lipid nanoparticles,[5,6] for interactions with lipid membrane components, including phospholipids[7] and cholesterol,[8] and for interactions with membrane proteins, whose extraction from such membranes was very recently reported by Chang *et al.* using carbohydrate-modified steroid skeletons.[9] Of the macrocyclic platforms available, the strong capacity of cyclodextrins to complex with membrane lipids,[10] or to undergo intermolecular inclusion of hydrophobic pendant functions,[11,12] makes them somewhat less interesting for complexation with membrane proteins or peptides than the calix[*n*]arene or resorcinarene platforms.

Amphiphilic calix[*n*]arenes[13,14] and resorcinarenes[15] are well known, and their capacity to form self-assembled structures, such as solid lipid nanoparticles[6] or monomolecular films,[13] has been demonstrated. Such systems have been shown by ourselves[16,17] and Schrader *et al.*[18] to interact with various soluble proteins. We are currently developing micellar systems based on calix[4]arenes for interaction with membrane proteins. The geometric requirements for the formation of micelles by amphiphiles involves, at least for simple molecules, the construction of conical molecular shapes, with control over the ratio of polar head group size to the length of the hydrophobic chain.[19] For this reason, we have concentrated on using calix[4]arenes that are monosubstituted at the phenolic face by alkyl chains of varying length, and on using the quinonemethide synthesis to introduce polar groups *para* to the unsubstituted phenolic groups.[20]

A side effect of the choice of this synthetic route is that only three methylene groups will be present at the *para*-position, and in contrast to both tetramethylenesulfonate-calix-[4]-arene[21] and the tetra-*para*-alkyl-calix[4]arenes,[22] it is hoped that the cavity is not fully closed, and remains available for interactions with amino acid side chains.

In a previous paper, we described the synthesis and self-assembly properties of tris[(dimethylamino)methyl]-25-mono-alkoxy-26,27,28-trihydroxycalix[4]arene derivatives; however, these molecules present problems for the formation of well defined micelles at physiological pH values between pH 7 and 8.[20] In this paper we describe the synthesis of a series of tris[(carboxy)methyl]-25-monoalkoxy-26,27,28-trihydroxycalix[4]-arene derivatives and the self-assembly properties of these systems to yield micellar systems at physiological pH values. The solid-state structures of four intermediate tris[(cyano)methyl]-25-mono-alkoxy-26,27,28-trihydroxycalix[4]arene derivatives show the inclusion of solvent for derivatives with short alkyl chains and the formation of 1-D inclusion polymers for derivatives with longer alkyl substituents.

Experimental section

General

Calix[4]arenes, **1a–k** were synthesised as per the literature.[20] Reagents were purchased from Sigma-Aldrich and ACROS, and

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used without further purification. All solvents were distilled under a nitrogen atmosphere over an appropriate drying agent immediately prior to use. All reactions were carried out under nitrogen.

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXP 300 instrument operating at 500 and 125 MHz, respectively. The chemical shifts are reported from an internal tetramethylsilane standard for spectra in $CDCl_3$ and from H_2O for spectra recorded in DMSO-d_6. Melting point measurements were performed on a Beotius apparatus and are uncorrected.

Surface tension measurements were carried out on a Kibron μ-trough and are quoted as the mean of three measurements. All measurements were carried out at 20 °C. Each suspension was allowed to come to equilibrium over 30 min.

Synthesis of the 5,11,17-tris[(cyano)methyl]-25-monoalkoxy-26,27,28-trihydroxycalix[4]arenes, 2a–2k. To the compounds of series **1** (0.016 mol) in 180 mL of DMSO was added 3.05 equiv. of CH_3I. The mixture was stirred for 30 min at room temperature, after which time 10 equiv. of NaCN was added and the mixture heated for 3 h at 80 °C under an atmosphere of N_2. The solution was cooled, treated with ice water, acidified with 2 N HCl and filtered. The residue was treated with 200 ml of $CHCl_3$ and 300 ml water, and the organic layer separated and washed three times with 250 ml portions of water. The $CHCl_3$ solution was dried over $MgSO_4$ and then evaporated to leave a crude product, which was washed with hexane (100 ml) to give the desired product.

5,11,17-Tris[(cyano)methyl]-25-monomethoxy-26,27,28-trihydroxycalix[4]arene (2a). Yield 70%, pale yellow solid, mp > 250 °C. IR: ν = 3180 (O–H), 2940 (C–H), 2249 (C≡N), 1600 (C=C), 1455 (C–H) and 1079 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.37 (d, 2H, $^3J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 3.49 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 3.55 (s, 6H, Ar–CH_2–CN), 4.15 (s, 3H, Ar–OCH_3), 4.24 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 4.35 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 6.92 (s, 3H, Ar–*H*), 7.03 (s, 3H, Ar–*H*), 7.11 (s, 3H, Ar–*H*), 9.37 (s, 2H, Ar–O*H*) and 9.67 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 22.5 (Ar–*C*H_2–CN), 31.0, 31.5 (Ar–*C*H_2–Ar), 63.4 (Ar–O*C*H_3), 117.9 (Ar–CH$_2$–*C*N), 121.9, 126.3, 127.9, 128.1, 128.5, 129.0, 129.2, 129.4, 133.5 (Ar), 149.3, 150.2 (Ar*C*–OH) and 152.3 (Ar*C*–OCH$_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): *m*/*z* = 556.1 [M + H]$^+$, 578.1 [M + Na]$^+$ and 594.0 [M + K]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monoethoxy-26,27,28-trihydroxycalix[4]arene (2b). Yield 73%, yellow solid, mp = 205 °C. IR: ν = 3160 (O–H), 2940 (C–H), 2249 (C≡N), 1590 (C=C), 1460 (C–H) and 1085 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.78 (t, 3H, $^3J_{H-H}$ = 7.1 Hz, Ar–OCH$_2$CH_3), 3.48 (d, 4H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.55 (s, 6H, Ar–C-H_2–CN), 4.28 (q, 2H, $^3J_{H-H}$ = 7.1 Hz, Ar–OCH_2CH$_3$), 4.30 (d, 4H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.91–7.14 (m, 9H, Ar–*H*), 9.48 (s, 2H, Ar–O*H*) and 9.82 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 15.4 (Ar–OCH$_2$*C*H$_3$), 22.9 (Ar–*C*H$_2$–CN), 31.3, 31.9 (Ar–*C*H$_2$–Ar), 73.1 (Ar–O*C*H$_2$CH$_3$), 118.3 (Ar–CH$_2$–*C*N), 122.3, 123.2, 126.5, 126.6, 128.2, 128.4, 128.5, 128.8, 128.9, 129.1, 129.4, 129.6, 134.2 (Ar), 149.4, 150.6 (Ar*C*–OH) and 151.4 Ar*C*–OCH$_2$CH$_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): *m*/*z* = 570.2 [M + H]$^+$ and 592.0 [M + Na]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monopropoxy-26,27,28-trihydroxycalix[4]arene (2c). Yield 81%, yellow solid, mp = 156 °C. IR: ν = 3164 (O–H), 2940 (C–H), 2249 (C≡N), 1600 (C=C), 1456 (C–H) and 1078 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, Ar–O(CH$_2$)$_2$CH_3), 2.19 (m, 2H, Ar–OCH$_2$CH_2CH$_3$), 3.43 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.46 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.54 (s, 6H, Ar–CH_2–CN), 4.11 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, Ar–OCH_2CH$_2$CH$_3$), 4.24 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.34 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.90–7.10 (m, 9H, Ar–*H*), 9.42 (s, 2H, Ar–O*H*) and 9.66 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 10.9 (Ar–O(CH$_2$)$_2$*C*H$_3$), 23.0 (Ar–*C*H$_2$–CN), 23.5 (Ar–OCH$_2$*C*H$_2$CH$_3$), 31.6, 32.0 (Ar–*C*H$_2$–Ar), 79.5 (Ar–O*C*H$_2$CH$_2$CH$_3$), 118.4 (Ar–CH$_2$–*C*N), 122.3, 123.4, 126.6, 128.3, 128.5, 128.6, 128.8, 129.5, 129.7, 134.1 (Ar), 149.4, 150.8 (Ar*C*–OH) and 151.7 (Ar*C*–O(CH$_2$)$_2$CH$_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): *m*/*z* = 584.1 [M + H]$^+$ and 606.1 [M + Na]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monobutoxy-26,27,28-trihydroxycalix[4]arene (2d). Yield 69%, yellow solid, mp = 156 °C. IR: ν = 3160 (O–H), 2940 (C–H), 2249 (C≡N), 1600 (C=C), 1457 (C–H) and 1078 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.14 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, Ar–O(CH$_2$)$_3$CH_3), 1.72 (m, 2H, Ar–O(CH$_2$)$_2$CH_2CH$_3$), 2.16 (m, 2H, Ar–OCH$_2$C-H_2CH$_2$CH$_3$), 3.45 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.53 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH$_2$–Ar), 3.57 (s, 6H, Ar–CH_2–CN), 4.17 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, Ar–CH_2(CH$_2$)$_2$CH$_3$), 4.27 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.36 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.93–7.12 (m, 9H, Ar–*H*), 9.47 (s, 2H, Ar–O*H*) and 9.73 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.1 (Ar–O(CH$_2$)$_3$*C*H$_3$), 19.3 (Ar–O(CH$_2$)$_2$-*C*H$_2$CH$_3$), 22.8 (Ar–*C*H$_2$–CN), 31.4 (Ar–OCH$_2$*C*H$_2$CH$_2$CH$_3$), 31.8, 32.0 (Ar–*C*H$_2$–Ar), 77.5 (Ar–O*C*H$_2$(CH$_2$)$_2$CH$_3$), 118.3 (Ar–CH$_2$–*C*N), 122.1, 123.2, 126.4, 128.1, 128.3, 128.5, 128.7, 129.3, 129.5, 133.9 (Ar), 149.2, 150.6 (Ar*C*–OH) and 151.5 (Ar*C*–O(CH$_2$)$_3$CH$_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): *m*/*z* = 620.2 [M + Na]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monopentoxy-26,27,28-trihydroxycalix[4]arene (2e). Yield 77%, yellow-brown solid, mp = 155 °C. IR: ν = 3186 (O–H), 2940 (C–H), 2248 (C≡N), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.02 (t, 3H, $^3J_{H-H}$ = 7.2 Hz, Ar–O(CH$_2$)$_4$CH_3), 1.52 (m, 2H, Ar–O(CH$_2$)$_3$CH_2CH$_3$), 1.63 (m, 2H, Ar–O(CH$_2$)$_2$CH_2CH$_2$CH$_3$), 2.15 (m, 2H, Ar–OCH$_2$CH_2(CH$_2$)$_2$CH$_3$), 3.42 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.49 (d, 2H, , $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.54 (s, 6H, Ar–CH_2–CN), 4.14 (t, 2H, $^3J_{H-H}$ = 6.9 Hz, Ar–OCH_2(CH$_2$)$_3$CH$_3$), 4.24 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.33 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.91–7.09 (m, 9H, Ar–*H*), 9.42 (s, 2H, Ar–O*H*) and 9.67 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 15.4 (Ar–O(CH$_2$)$_4$*C*H$_3$), 22.7 (Ar–O(CH$_2$)$_3$*C*H$_2$CH$_3$), 22.9 (Ar–*C*H$_2$–CN), 28.5 (Ar–O(CH$_2$)$_2$-*C*H$_2$CH$_2$CH$_3$), 29.8 (Ar–OCH$_2$*C*H$_2$(CH$_2$)$_2$CH$_3$), 31.6, 31.9 (Ar–CH$_2$–Ar), 77.5 (Ar–O*C*H$_2$(CH$_2$)$_3$CH$_3$), 118.3 (Ar–CH$_2$–*C*N), 122.3, 123.2, 126.5, 126.6, 128.2, 128.4, 128.8, 128.9, 129.1, 129.4, 129.6, 134.2 (Ar), 149.4, 150.6 (Ar*C*–OH) and

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151.4 (Ar*C*–O(CH_2)$_4$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = 612.2 [M + H]$^+$, 634.1 [M + Na]$^+$ and 650.2 [M + K]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monohexoxy-26,27,28-trihydroxycalix[4]arene (2f). Yield 81%, yellow-brown solid, mp = 125 °C. IR: ν = 3165 (O–H), 2930 (C–H), 2249 (C≡N), 1600 (C=C), 1457 (C–H) and 1080 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.96 (t, 3H, $^3J_{H-H}$ = 6.8 Hz, Ar–O(CH_2)$_5$$CH_3$), 1.45 (m, 4H, Ar–O($CH_2$)$_3$$CH_2$$CH_2$$CH_3$), 1.66 (m, 2H, Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_2$$CH_3$), 2.14 (m, 2H, Ar–$CH_2$$CH_2$($CH_2$)$_3$$CH_3$), 3.42 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 3.49 (d, 2H, , $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.54 (s, 6H, Ar–CH_2–CN), 4.12 (t, 2H, $^3J_{H-H}$ = Hz, Ar–OCH_2(CH_2)$_4$$CH_3$), 4.24 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 4.33 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 6.91–7.09 (m, 9H, Ar–*H*), 9.44 (s, 2H, Ar–O*H*) and 9.69 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.2 (Ar–O(CH_2)$_5$$CH_3$), 22.7 (Ar–O($CH_2$)$_4$$CH_2$$CH_3$), 22.9 (Ar–$CH_2$–CN), 25.7 (Ar–O($CH_2$)$_3$$CH_2$$CH_2$$CH_3$), 30.0 (Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_2$$CH_3$), 31.2 (Ar–O$CH_2$$CH_2$($CH_2$)$_3$$CH_3$), 31.5, 31.9 (Ar–$CH_2$–Ar), 77.8 (Ar–O$CH_2$($CH_2$)$_4$$CH_3$), 118.2 (Ar–$CH_2$–CN), 122.2, 123.2, 123.8, 126.6, 127.8, 128.1, 128.4, 128.8, 129.4, 130.1, 133.9 (Ar), 149.4, 150.7 (Ar*C*–OH) and 151.7 (Ar*C*–O(CH_2)$_5$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = 626.3 [M + H]$^+$ and 648.1 [M + Na]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monoheptoxy-26,27,28-trihydroxycalix[4]arene (2g). Yield 87%, brown solid, mp = 126 °C. IR: ν = 3180 (O–H), 2930 (C–H), 2250 (C≡N), 1600 (C=C), 1460 (C–H) and 1078 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 3H, $^3J_{H-H}$ = 6.9 Hz, Ar–O(CH_2)$_6$$CH_3$), 1.36 (m, 4H, Ar–O($CH_2$)$_4$$CH_2$$CH_2$$CH_3$), 1.49 (m, 2H, Ar–O($CH_2$)$_3$$CH_2$($CH_2$)$_2$$CH_3$), 1.63 (m, 2H, Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_3$$CH_3$), 2.14 (m, 2H, Ar–O$CH_2$$CH_2$($CH_2$)$_4$$CH_3$), 3.42 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.49 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.53 (s, 6H, Ar–CH_2–CN), 4.11 (t, 2H, $^3J_{H-H}$ = 7.1 Hz, Ar–OCH_2(CH_2)$_5$$CH_3$), 4.23 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.33 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.89–7.09 (m, 9H, Ar–*H*), 9.46 (s, 2H, Ar–O*H*) and 9.71 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.1 (Ar–O(CH_2)$_6$$CH_3$), 19.3 (Ar–O($CH_2$)$_5$$CH_2$$CH_3$), 22.6 (Ar–O($CH_2$)$_4$$CH_2$$CH_2$$CH_3$), 22.8 (Ar–$CH_2$–CN), 25.8 (Ar–O($CH_2$)$_3$$CH_2$($CH_2$)$_2$$CH_3$), 29.1 (Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_3$$CH_3$), 29.9 (Ar–O$CH_2$$CH_2$($CH_2$)$_4$$CH_3$), 31.4, 32.0 (Ar–$CH_2$–Ar), 77.5 (Ar–O$CH_2$($CH_2$)$_5$$CH_3$), 118.3 (Ar–$CH_2$–CN), 122.1, 123.2, 126.4, 128.3, 128.5, 128.7, 129.4, 129.5, 133.9 (Ar), 149.2 , 150.6 (Ar*C*–OH) and 151.5 (Ar*C*–O(CH_2)$_6$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = 640.0 [M + H]$^+$, 662.1 [M + Na]$^+$ and 678.1 [M + K]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monooctoxy-26,27,28-trihydroxycalix[4]arene (2h). Yield 85%, brown solid, mp = 127 °C. IR: ν = 3182 (O–H), 2926 (C–H), 2249 (C≡N), 1600 (C=C), 1460 (C–H) and 1079 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $^3J_{H-H}$ = 6.4 Hz, Ar–O(CH_2)$_7$$CH_3$), 1.34 (m, 4H, Ar–O($CH_2$)$_5$$CH_2$$CH_2$$CH_3$), 1.41 (m, 2H, Ar–O($CH_2$)$_4$$CH_2$($CH_2$)$_2$$CH_3$), 1.48 (m, 2H, Ar–O($CH_2$)$_3$$CH_2$($CH_2$)$_3$$CH_3$), 1.66 (m, 2H, Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_4$$CH_3$), 2.16 (m, 2H, Ar–O$CH_2$$CH_2$($CH_2$)$_5$$CH_3$), 3.44 (d, 4H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.50 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.56 (s, 6H, Ar–CH_2–CN), 4.14 (t, 2H, $^3J_{H-H}$ = 6.8 Hz, Ar–OCH_2(CH_2)$_6$$CH_3$), 4.25 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.34 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.91–7.11 (m, 9H, Ar–*H*), 9.47 (s, 2H, Ar–O*H*) and 9.72 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.3 (Ar–O(CH_2)$_7$$CH_3$), 22.8 (Ar–O($CH_2$)$_5$$CH_2$–$CH_2$$CH_3$), 22.9 (Ar–$CH_2$–CN), 26.0 (Ar–O($CH_2$)$_5$$CH_2$$CH_2$$CH_3$), 29.4 (Ar–O($CH_2$)$_4$$CH_2$($CH_2$)$_2$$CH_3$), 29.5 (Ar–O($CH_2$)$_3$–$CH_2$($CH_2$)$_3$$CH_3$), 30.0 (Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_4$$CH_3$), 31.1 (Ar–O$CH_2$$CH_2$($CH_2$)$_5$$CH_3$), 31.5, 31.9 (Ar–$CH_2$–Ar), 77.9 (Ar–O$CH_2$($CH_2$)$_6$$CH_3$), 118.3 (Ar–$CH_2$–CN), 122.2, 123.3, 126.5, 128.2, 128.5, 128.8, 129.4, 129.6, 134.0 (Ar), 149.3, 150.7 (Ar*C*–OH) and 151.6 (Ar*C*–O(CH_2)$_7$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = 654.3 [M + H]$^+$ and 676.2 [M + Na]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monononoxy-26,27,28-trihydroxycalix[4]arene (2i). Yield 86%, brown solid, mp = 148 °C. IR: ν = 3180 (O–H), 2930 (C–H), 2249 (C≡N), 1600 (C=C), 1460 (C–H) and 1078 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, Ar–O(CH_2)$_8$$CH_3$), 1.29 (m, 6H, Ar–O($CH_2$)$_5$$CH_2$$CH_2$$CH_2$$CH_3$), 1.32 (m, 2H, Ar–O($CH_2$)$_4$$CH_2$($CH_2$)$_3$$CH_3$), 1.35 (m, 2H, Ar–O($CH_2$)$_3$C–$H_2$($CH_2$)$_4$$CH_3$), 1.66 (m, 2H, Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_5$$CH_3$), 2.14 (m, 2H, Ar–O$CH_2$$CH_2$($CH_2$)$_6$$CH_3$), 3.42 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.49 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.54 (s, 6H, Ar–CH_2–CN), 4.13 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, Ar–OCH_2(CH_2)$_8$$CH_3$), 4.24 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.33 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.89–7.09 (m, 9H, Ar–*H*), 9.42 (s, 2H, Ar–O*H*) and 9.67 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.2 (Ar–O(CH_2)$_8$$CH_3$), 22.6 (Ar–O($CH_2$)$_7$$CH_2$$CH_3$), 22.8 (Ar–$CH_2$–CN), 25.9 (Ar–O($CH_2$)$_6$$CH_2$$CH_2$$CH_3$), 29.3 (Ar–O($CH_2$)$_5$$CH_2$($CH_2$)$_2$$CH_3$), 29.5 (Ar–O($CH_2$)$_4$$CH_2$($CH_2$)$_3$$CH_3$), 29.6 (Ar–O($CH_2$)$_3$$CH_2$–($CH_2$)$_4$$CH_3$), 29.9 (Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_5$$CH_3$), 31.4 (Ar–O$CH_2$$CH_2$($CH_2$)$_6$$CH_3$), 31.8, 31.9 (Ar–$CH_2$–Ar), 77.8 (Ar–O$CH_2$($CH_2$)$_7$$CH_3$), 118.1 (Ar–$CH_2$–CN), 122.1, 123.1, 126.4, 128.1, 128.3, 128.4, 128.6, 129.3, 129.4, 129.5, 133.9 (Ar), 149.2, 150.6 (Ar*C*–OH) and 151.5 (Ar*C*–O(CH_2)$_8$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = 668.1 [M + H]$^+$, 690.1 [M + Na]$^+$ and 706.2 [M + K]$^+$.

5,11,17-Tris[(cyano)methyl]-25-monodecoxy-26,27,28-trihydroxycalix[4]arene (2j). Yield 89%, brown solid, mp = 147 °C. IR: ν = 3160 (O–H), 2930 (C–H), 2249 (C≡N), 1600 (C=C), 1457 (C–H) and 1079 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.79 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, Ar–O(CH_2)$_9$$CH_3$), 1.20 (m, 6H, Ar–O($CH_2$)$_6$$CH_2$$CH_2$$CH_2$$CH_3$), 1.24 (m, 2H, Ar–O($CH_2$)$_5$$CH_2$($CH_2$)$_3$$CH_3$), 1.33 (m, 2H, Ar–O($CH_2$)$_4$–$CH_2$($CH_2$)$_4$$CH_3$), 1.42 (m, 2H, Ar–O($CH_2$)$_3$$CH_2$($CH_2$)$_5$$CH_3$), 1.66 (m, 2H, Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_6$$CH_3$), 2.08 (m, 2H, Ar–O$CH_2$$CH_2$($CH_2$)$_7$$CH_3$), 3.37 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 3.43 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.47 (s, 6H, Ar–CH_2–CN), 4.06 (t, 2H, $^3J_{H-H}$ = 6.9 Hz, Ar–OCH_2(CH_2)$_8$$CH_3$), 4.16 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 4.26 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 6.82–7.02 (m, 9H, Ar–*H*), 9.36 (s, 2H, Ar–O*H*) and 9.61 s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.2 (Ar–O(CH_2)$_9$$CH_3$), 22.8 (Ar–O($CH_2$)$_8$$CH_2$$CH_3$), 22.9 (Ar–$CH_2$–CN), 26.0 (Ar–O($CH_2$)$_7$$CH_2$$CH_2$$CH_3$), 29.5

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(Ar–O(CH_2)$_6$$CH_2$($CH_2$)$_2$$CH_3$), 29.6 (Ar–O($CH_2$)$_5$$CH_2$($CH_2$)$_3$-$CH_3$), 29.7 (Ar–O($CH_2$)$_4$$CH_2$($CH_2$)$_4$$CH_3$), 29.8 (Ar–O($CH_2$)$_3$-$CH_2$($CH_2$)$_5$$CH_3$), 30.0 (Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_6$$CH_3$), 31.5 (Ar–O$CH_2$$CH_2$($CH_2$)$_7$$CH_3$), 31.9, 32.0 (Ar–$CH_2$–Ar), 77.8 (Ar–O$CH_2$($CH_2$)$_8$$CH_3$), 118.1 (Ar–$CH_2$–CN), 122.1, 123.2, 126.4, 128.1, 128.3, 128.5, 128.7, 129.4, 129.5, 129.6, 134.0 (Ar), 149.2, 150.6 (Ar*C*–OH) and 151.6 (Ar*C*–O(CH_2)$_9$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = $[M + H]^+$, $[M + Na]^+$ and $[M + K]^+$.

5,11,17-Tris[(cyano)methyl]-25-monododecoxy-26,27,28-trihydroxycalix[4]arene (2k). Yield 89%, brown solid, mp = 147 °C. IR: ν = 3160 (O–H), 2930 (C–H), 2249 (C≡N), 1600 (C=C), 1460 (C–H) and 1079 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.79 (t, 3H, $^3J_{H-H}$ = 6.5 Hz, Ar–O(CH_2)$_{11}$$CH_3$), 1.19 (m, 6H, Ar–O($CH_2$)$_8$$CH_2$$CH_2$$CH_2$$CH_3$), 1.26 (m, 4H, Ar–O($CH_2$)$_6$$CH_2$$CH_2$($CH_2$)$_3$$CH_3$), 1.34 (m, 2H, Ar–O($CH_2$)$_5$$CH_2$($CH_2$)$_5$$CH_3$), 1.42 (m, 2H, Ar–O($CH_2$)$_4$ CH_2(CH_2)$_6$$CH_3$), 1.51 (m, 2H, Ar–O($CH_2$)$_3$$CH_2$($CH_2$)$_7$$CH_3$), 1.51 (m, 4H, Ar–O($CH_2$)$_2$$CH_2$($CH_2$)$_8$$CH_3$), 1.59 (m, 2H, Ar–O$CH_2$$CH_2$($CH_2$)$_9$$CH_3$), 3.38 (d, 4H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.48 (s, 6H, Ar–CH_2–CN), 4.07 (t, 2H, $^3J_{H-H}$ = Hz, Ar–OCH_2(CH_2)$_{10}$$CH_3$), 4.17 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.27 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.85–7.03 (m, 9H, Ar–*H*), 9.38 (s, 2H, Ar–O*H*) and 9.63 (s, 1H, Ar–O*H*). ^{13}C NMR ($CDCl_3$): δ 14.2 (Ar–O(CH_2)$_{11}$-CH_3), 22.8 (Ar–O(CH_2)$_{10}$$CH_2$$CH_3$), 22.9 (Ar–$CH_2$–CN), 26.0 (Ar–O($CH_2$)$_8$$CH_2$($CH_2$)$_2$$CH_3$), 29.5 (Ar–O($CH_2$)$_9$-$CH_2$$CH_2$$CH_3$), 29.6 (Ar–O($CH_2$)$_7$$CH_2$($CH_2$)$_3$$CH_3$), 29.7 (Ar–O($CH_2$)$_6$$CH_2$($CH_2$)$_4$$CH_3$), 29.8 (Ar–O($CH_2$)$_5$$CH_2$-($CH_2$)$_5$$CH_3$), 29.9 (Ar–O($CH_2$)$_4$$CH_2$($CH_2$)$_6$$CH_3$), 30.0 (Ar–O($CH_2$)$_3$$CH_2$($CH_2$)$_7$$CH_3$), 30.1 (Ar–O($CH_2$)$_2$$CH_2$-($CH_2$)$_8$$CH_3$), 31.5 (Ar–O$CH_2$$CH_2$($CH_2$)$_9$$CH_3$), 31.9, 32.0 (Ar–$CH_2$–Ar), 78.0 (Ar–O$CH_2$($CH_2$)$_{10}$$CH_3$), 118.2 (Ar–$CH_2$–CN), 122.1, 126.1, 128.1, 128.3, 128.5, 128.7, 129.4, 129.5, 129.6, 134.0 (Ar), 149.2, 150.6 (Ar*C*–OH) and 151.6 Ar-*C*–O(CH_2)$_{11}$$CH_3$). ES mass spectrum ($CHCl_3$/MeOH 1 : 1, HCOOH 1%): m/z = 710.3 $[M + H]^+$ and 732.3 $[M + Na]^+$.

Synthesis of 5,11,17-tris[(carboxy)methyl]-25-monoalkoxy-26,27,28-trihydroxycalix[4]arenes, 3a–3k. A mixture of the compounds of series **2** (7 mmol) and KOH (8 equiv.) in 200 mL of a 1 : 2 water/ethanol mixture was heated under reflux for 72 h. The mixture was then cooled to room temperature, filtered and neutralized with 20% HCl to give a precipitate that was removed by filtration, washed with 0.1 M HCl and dried to give the desired product.

5,11,17-Tris[(carboxy)methyl]-25-monomethoxy-26,27,28-trihydroxycalix[4]arene (3a). Yield 70%, creamy solid, mp > 250 °C. IR: ν = 3160 (O–H), 2940 (C–H), 1700 (C=O), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^{1}H NMR (DMSO): δ 3.31 (s, 6H, Ar–CH_2–COOH), 3.39 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 3.48 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 4.01 (s, 3H, Ar–OCH_3), 4.18 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 4.25 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 6.95–7.15 (m, 9H, Ar–*H*), 8.80 (s, 2H, Ar–*H*), 9.50 (s, 1H, Ar–*H*) and 12.18 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): 30.4, 30.9 (Ar–CH_2–Ar), 39.6 (Ar–CH_2–COOH), 63.6 (Ar–OCH_3), 125.5, 126.5, 128.1, 129.4, 129.6, 133.9 (Ar), 148.2, 149.9 (Ar*C*–OH), 153.4 (Ar*C*–OCH_3) and 172.9 (Ar–CH_2*C*OOH). ES mass spectrum (DMSO): m/z = 613.1 $[M + H]^+$, 635.1 $[M + Na]^+$ and 611.3 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monoethoxy-26,27,28-trihydroxycalix[4]arene (3b). Yield 73%, creamy solid, mp > 250 °C. IR: ν = 3160 (O–H), 2930 (C–H), 1700 (C=O), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^{1}H NMR (DMSO): δ 1.62 (t, 3H, $^3J_{H-H}$ = 7.2 Hz, Ar–O$CH_2$$CH_3$), 3.16 (s, 6H, Ar–$CH_2$–COOH), 3.30 (d, 2H, $^2J_{H-H}$ = 12.1 Hz, Ar–CH_2–Ar), 3.47 (d, 2H, $^2J_{H-H}$ = 12.1 Hz, Ar–CH_2–Ar), 4.15 (q, 2H, $^3J_{H-H}$ = 7.2 Hz, Ar–O$CH_2$$CH_3$), 4.18 (d, 2H, $^2J_{H-H}$ = 12.1 Hz, Ar–CH_2–Ar), 4.22 (d, 2H, $^2J_{H-H}$ = 12.1 Hz, Ar–CH_2–Ar), 6.85–7.14 (m, 9H, Ar–*H*), 8.93 (s, 2H, Ar–O*H*), 9.57 (s, 1H, Ar–O*H*) and 12.14 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 15.0 (Ar–O$CH_2$$CH_3$), 30.4, 30.6 (Ar–$CH_2$–Ar), 39.7 (Ar–$CH_2$–COOH) 72.7 (Ar–O$CH_2$$CH_3$), 126.5, 127.9, 128.1, 129.0, 129.4, 133.9 (Ar), 148.0, 149.5 (Ar*C*–OH), 151.6 (Ar*C*–O$CH_2$$CH_3$) and 172.8 (Ar–$CH_2$–*C*OOH). ES mass spectrum (DMSO): m/z = 627.1 $[M + H]^+$, 649.0 $[M + Na]^+$, and 625.1 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monopropoxy-26,27,28-trihydroxycalix[4]arene (3c). Yield 78%, creamy solid, mp = 198 °C. IR: ν = 3160 (O–H), 2940 (C–H), 1700 (C=O), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^{1}H NMR (DMSO): δ 1.24 (t, 3H, $^3J_{H-H}$ = 7.2 Hz, Ar–O$CH_2$$CH_2$$CH_3$), 2.03 (m, 2H, Ar–O$CH_2$$CH_2$$CH_3$), 3.17 (s, 6H, Ar–$CH_2$–COOH), 3.32 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 3.48 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 4.02 (t, 2H, $^3J_{H-H}$ = 7.2 Hz, Ar–O$CH_2$$CH_2$$CH_3$), 4.17 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 4.22 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 6.84–7.17 (m, 9H, Ar–*H*), 8.88 (s, 2H, Ar–O*H*), 9.54 (s, 1H, Ar–O*H*) and 12.17 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 10.5 (Ar–O(CH_2)$_2$$CH_3$), 22.7 (Ar–O$CH_2$$CH_2$$CH_3$), 30.2, 30.5 (Ar–$CH_2$–Ar), 39.7 (Ar–$CH_2$–COOH), 78.8 (Ar–O$CH_2$$CH_2$$CH_3$), 125.3, 126.2, 127.6, 127.8, 128.9, 129.1, 129.3, 133.8 (Ar), 147.8, 149.9 (Ar*C*–OH), 151.8 (Ar–O$CH_2$$CH_2$$CH_3$) and 172.9 (Ar–$CH_2$–*C*OOH). ES mass spectrum (DMSO): m/z = 641.1 $[M + H]^+$, 663.0 $[M + Na]^+$ and 639.1 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monobutoxy-26,27,28-trihydroxycalix[4]arene (3d). Yield 75%, creamy solid, mp = 192 °C. IR: ν = 3160 (O–H), 2940 (C–H), 1700 (C=O), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^{1}H NMR (DMSO): δ 1.07 (t, 3H, $^3J_{H-H}$ = 7.2 Hz, Ar–O(CH_2)$_3$$CH_3$), 1.69 (m, 2H, Ar–O($CH_2$)$_2$$CH_2$$CH_3$), 2.01 (m, 2H, Ar–O$CH_2$C-$H_2$$CH_2$$CH_3$), 3.22 (s, 6H, Ar–$CH_2$–COOH), 3.37 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 3.46 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 4.05 (t, 2H, $^3J_{H-H}$ = 7.2 Hz, Ar–OCH_2(CH_2)$_2$$CH_3$), 4.16 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–C-H_2–Ar), 4.22 (d, 2H, $^2J_{H-H}$ = 13.6 Hz, Ar–CH_2–Ar), 6.82–7.12 (m, 9H, Ar–*H*), 8.87 (s, 2H, Ar–O*H*), 9.56 (s, 1H, Ar–O*H*) and 12.16 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 14.3 (Ar–O(CH_2)$_3$$CH_3$), 18.7 (Ar–O($CH_2$)$_2$-$CH_2$$CH_3$), 30.3 (Ar–O$CH_2$$CH_2$$CH_2$$CH_3$), 30.7, 31.4 (Ar–$CH_2$–Ar), 39.7 (Ar–$CH_2$–COOH), 76.6 (Ar–O$CH_2$($CH_2$)$_2$-$CH_3$), 125.7, 127.6, 128.7, 129.3, 130.1, 134.0 (Ar), 147.8, 150.0 (Ar*C*–OH), 151.9 (Ar*C*–O(CH_2)$_3$$CH_3$) and 172.9

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(Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z = 655.2 $[M + H]^+$, 677.1 $[M + Na]^+$ and 653.1 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monopentoxy-26,27,28-trihydroxycalix[4]arene (3e). Yield 72%, creamy solid, mp = 190 °C. IR: ν = 3160 (O–H), 2940 (C–H), 1700 (C═O), 1600 (C═C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.99 (t, 3H, $^3J_{H-H}$ = 7.1 Hz, Ar–$O(CH_2)_4CH_3$), 1.47 (m, 2H, Ar–$O(CH_2)_3CH_2CH_3$), 1.62 (m, 2H, Ar–$O(CH_2)_2CH_2CH_2CH_3$), 2.02 (m, 2H, Ar–$OCH_2CH_2(CH_2)_2CH_3$), 3.23 (s, 6H, Ar–CH_2–COOH), 3.38 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 3.47 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 4.15 (t, 2H, $^3J_{H-H}$ = 7.1 Hz, Ar–$OCH_2(CH_2)_3CH_3$), 4.21 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 4.23 (d, 2H, $^2J_{H-H}$ = 13.4 Hz, Ar–CH_2–Ar), 6.85–7.14 (m, 9H, Ar–*H*), 8.93 (s, 2H, Ar–O*H*), 9.57 (s, 1H, Ar–O*H*) and 12.14 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 13.9 (Ar–$O(CH_2)_4CH_3$), 21.9 (Ar–$O(CH_2)_3CH_2CH_3$), 27.3 (Ar–$O(CH_2)_2CH_2CH_2H_3$), 28.9 (Ar–$OCH_2CH_2(CH_2)_2CH_3$), 30.4, 30.6 (Ar–CH_2–Ar), 39.6 (Ar–CH_2–COOH), 77.2 (Ar–$OCH_2(CH_2)_3CH_3$), 125.4, 126.3, 127.7, 128.1, 129.0, 129.2, 129.4, 134.2 (Ar), 147.8, 150.3 (Ar*C*–OH) and 152.2 (Ar*C*–$O(CH_2)_4CH_3$). ES mass spectrum (DMSO): m/z = 668.1 $[M]^+$, 691.1 $[M + Na]^+$ and 667.0 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monohexoxy-26,27,28-trihydroxycalix[4]arene (3f). Yield 79%, creamy solid, mp = 182 °C. IR: ν = 3180 (O–H), 2930 (C–H), 1700 (C═O), 1600 (C═C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.94 (t, 3H, $^3J_{H-H}$ = 6.8 Hz, Ar–$O(CH_2)_5CH_3$), 1.42 (m, 4H, Ar–$O(CH_2)_3CH_2CH_2CH_3$), 1.67 (m, 2H, Ar–$O(CH_2)_2CH_2(CH_2)_2CH_3$), 2.02 (m, 2H, Ar–$CH_2CH_2(CH_2)_3CH_3$), 3.22 (s, 6H, Ar–$CH_2$–COOH), 3.37 (d, 2H, $^2J_{H-H}$ = 13.3 Hz, Ar–CH_2–Ar), 3.46 (d, 2H, $^2J_{H-H}$ = 13.3 Hz, Ar–CH_2–Ar), 4.04 (t, 2H, $^3J_{H-H}$ = 6.8 Hz, Ar–$OCH_2(CH_2)_4CH_3$), 4.16 (d, 2H, $^2J_{H-H}$ = 13.3 Hz, Ar–CH_2–Ar), 4.20 (d, 2H, $^2J_{H-H}$ = 13.3 Hz, Ar–CH_2–Ar), 6.87–7.12 (m, 9H, Ar–*H*), 8.88 (s, 2H, Ar–O*H*), 9.55 (s, 1H, Ar–O*H*) and 12.22 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 14.0 (Ar–$O(CH_2)_5CH_3$), 22.3 (Ar–$O(CH_2)_4CH_2CH_3$), 24.8 (Ar–$O(CH_2)_3CH_2CH_2CH_3$), 29.3 (Ar–$O(CH_2)_2CH_2(CH_2)_2CH_3$), 29.7 (Ar–$OCH_2CH_2(CH_2)_3CH_3$), 30.6, 31.01 (Ar–$CH_2$–Ar), 39.7 (Ar–$CH_2$–COOH), 77.2 (Ar–$OCH_2(CH_2)_4CH_3$), 125.4, 126.8, 127.9, 129.6, 134.0 (Ar), 147.8, 150.0 (Ar*C*–OH), 151.9 (Ar*C*–$O(CH_2)_5CH_3$) and 173.1 (Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z = 683.1 $[M + H]^+$, 705.1 $[M + Na]^+$ and 681.1 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monoheptoxy-26,27,28-trihydroxycalix[4]arene (3g). Yield 78%, creamy solid, mp = 160 °C. IR: ν = 3150 (O–H), 2930 (C–H), 1700 (C═O), 1600 (C═C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.91 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, Ar–$O(CH_2)_6CH_3$), 1.36 (m, 4H, Ar–$O(CH_2)_4CH_2CH_2CH_3$), 1.45 (m, 2H, Ar–$O(CH_2)_3CH_2(CH_2)_2CH_3$), 1.66 (m, 2H, Ar–$O(CH_2)_2CH_2(CH_2)_3CH_3$), 2.02 (m, 2H, Ar–$OCH_2CH_2(CH_2)_4CH_3$), 3.22 (s, 6H, Ar–$CH_2$–COOH), 3.31 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 3.47 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 3.99 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, Ar–$OCH_2(CH_2)_5CH_3$), 4.14 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 4.26 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 6.75–7.03 (m, 9H, Ar–*H*), 8.89 (s, 2H, Ar–O*H*), 9.54 (s, 1H, Ar–O*H*) and 12.22 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 13.9 (Ar–$O(CH_2)_6CH_3$), 21.9 (Ar–$O(CH_2)_5CH_2CH_3$), 24.9 (Ar–$O(CH_2)_4CH_2CH_2CH_3$), 28.2 (Ar–$O(CH_2)_3CH_2(CH_2)_2CH_3$), 29.1 (Ar–$O(CH_2)_2CH_2(CH_2)_3CH_3$), 30.1 (Ar–$OCH_2CH_2(CH_2)_4CH_3$), 30.9, 31.0 (Ar–$CH_2$–Ar), 39.7 (Ar–$CH_2$–COOH), 76.7 (Ar–$OCH_2(CH_2)_5CH_3$), 125.4, 126.4, 127.7, 127.9, 128.1, 129.2, 129.4, 133.9 (Ar), 147.5, 149.7 (Ar*C*–OH), 151.6 (Ar*C*–$O(CH_2)_6CH_3$) and 172.8 (Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z = 697.1 $[M + H]^+$, 719.1 $[M + Na]^+$ and 695.1 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monooctoxy-26,27,28-trihydroxycalix[4]arene (3h). Yield 80%, creamy solid, mp = 158 °C. IR: ν = 3190 (O–H), 2940 (C–H), 1700 (C═O), 1600 (C═C), 1440 (C–H) and 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.86 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, Ar–$O(CH_2)_7CH_3$), 1.31 (m, 6H, Ar–$O(CH_2)_4CH_2CH_2CH_2CH_3$), 1.43 (m, 2H, Ar–$O(CH_2)_3CH_2(CH_2)_3CH_3$), 1.66 (m, 2H, Ar–$O(CH_2)_2CH_2(CH_2)_4CH_3$), 2.01 (m, 2H, Ar–$OCH_2CH_2(CH_2)_5CH_3$), 3.22 (s, 6H, Ar–$CH_2$–COOH), 3.30 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 3.47 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 4.03 (t, 2H, $^3J_{H-H}$ = 6.0 Hz, Ar–$OCH_2(CH_2)_6CH_3$), 4.16 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 4.21 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, Ar–CH_2–Ar), 6.88–7.17 (m, 9H, Ar–*H*), 8.89 (s, 2H, Ar–O*H*), 9.53 (s, 1H, Ar–O*H*) and 12.23 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 13.4 (Ar–$O(CH_2)_7CH_3$), 21.4 (Ar–$O(CH_2)_6CH_2CH_3$), 23.9 (Ar–$O(CH_2)_5CH_2CH_2CH_3$), 27.6 (Ar–$O(CH_2)_4CH_2(CH_2)_2CH_3$), 28.9 (Ar–$O(CH_2)_3CH_2(CH_2)_3CH_3$), 29.6 (Ar–$O(CH_2)_2CH_2(CH_2)_4CH_3$), 30.3 (Ar–$OCH_2CH_2(CH_2)_5CH_3$), 30.8, 31.0 (Ar–$CH_2$–Ar), 39.6 (Ar–$CH_2$–COOH), 76.5 (Ar–$OCH_2(CH_2)_6CH_3$), 125.4, 126.3, 127.4, 127.9, 128.5, 129.3, 134.2 (Ar), 147.3, 149.6 (Ar*C*–OH), 151.5 (Ar*C*–$O(CH_2)_7CH_3$) and 172.5 (Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z = 711.0 $[M + H]^+$, 733.1 $[M + Na]^+$, 749.4 $[M + K]^+$ and 709.1 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monononoxy-26,27,28-trihydroxycalix[4]arene (3i). Yield 79%, creamy solid, mp > 250 °C. IR: ν = 3160 (O–H), 2930 (C–H), 1700 (C═O), 1600 (C═C), 1460 (C–H), 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.84 (t, 3H, $^3J_{H-H}$ = 6.1 Hz, Ar–$O(CH_2)_8CH_3$), 1.24 (m, 6H, Ar–$O(CH_2)_5CH_2CH_2CH_2CH_3$), 1.33 (m, 4H, Ar–$O(CH_2)_4CH_2CH_2(CH_2)_3CH_3$), 1.43 (m, 2H, Ar–$O(CH_2)_3CH_2(CH_2)_4CH_3$), 1.65 (m, 2H, Ar–$O(CH_2)_2CH_2(CH_2)_5CH_3$), 1.98 (m, 2H, Ar–$OCH_2CH_2(CH_2)_6CH_3$), 3.22 (s, 6H, Ar–$CH_2$–COOH), 3.32 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 3.46 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.01 (t, 2H, $^3J_{H-H}$ = 6.1 Hz, Ar–$OCH_2(CH_2)_7CH_3$), 4.17 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 4.21 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, Ar–CH_2–Ar), 6.83–7.17 (m, 9H, Ar–*H*), 8.89 (s, 2H, Ar–O*H*), 9.54 (s, 1H, Ar–O*H*) and 12.24 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 13.2 (Ar–$O(CH_2)_8CH_3$), 21.2 (Ar–$O(CH_2)_7CH_2CH_3$), 23.7 (Ar–$O(CH_2)_6CH_2CH_2CH_3$), 27.5 (Ar–$O(CH_2)_5CH_2(CH_2)_2CH_3$), 29.1 (Ar–$O(CH_2)_4CH_2(CH_2)_3CH_3$), 29.8 (Ar–$O(CH_2)_3CH_2(CH_2)_4CH_3$), 30.01 (Ar–$O(CH_2)_2CH_2(CH_2)_5CH_3$), 30.03 (Ar–$O(CH_2)_3CH_2(CH_2)_4CH_3$), 31.0, 31.2 (Ar–$CH_2$–Ar), 39.7 (Ar–$CH_2$–COOH), 76.4 (Ar–$OCH_2(CH_2)_7CH_3$), 125.3, 126.4, 127.1, 128.2, 128.7, 129.5, 134.2 (Ar), 148.1, 149.7 (Ar*C*–OH), 151.2 (Ar*C*–$O(CH_2)_8CH_3$) and 172.3 (Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z =

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725.0 $[M + H]^+$, 747.5 $[M + Na]^+$, 763.5 $[M + K]^+$ and 723.0 $[M - H]^-$.

5,11,17-Tris[(carboxy)methyl]-25-monodecoxy-26,27,28-trihydroxycalix[4]arene (3j). Yield 82%, creamy solid, mp = 150 °C. IR: ν = 3180 (O–H), 2930 (C–H), 1700 (C=O), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.84 (t, 3H, $^3J_{H-H}$ = 6.1 Hz, Ar–O(CH_2)$_9$CH_3), 1.25 (m, 6H, Ar–O(CH_2)$_6$CH_2CH_2CH_2CH_3), 1.31 (m, 4H, Ar–O(CH_2)$_4$-CH_2CH_2(CH_2)$_3$CH_3), 1.44 (m, 2H, Ar–O(CH_2)$_3$-CH_2(CH_2)$_5$CH_3), 1.66 (m, 2H, Ar–O(CH_2)$_2$CH_2(CH_2)$_6$CH_3), 2.01 (m, 2H, Ar–OCH_2CH_2(CH_2)$_7$CH_3), 3.22 (s, 6H, Ar–CH_2–COOH), 3.32 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 3.44 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 4.01 (t, 2H, $^3J_{H-H}$ = 7.1 Hz, Ar–OCH_2(CH_2)$_8$CH_3), 4.17 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 4.22 (d, 2H, $^2J_{H-H}$ = 13.2 Hz, Ar–CH_2–Ar), 6.83–7.19 (m, 9H, Ar–*H*), 8.90 (s, 2H, Ar–O*H*), 9.53 (s, 1H, Ar–O*H*) and 12.32 (s, 3H, Ar–CH_2–COO*H*). ^{13}C NMR (DMSO): δ 13.1 (Ar–O(CH_2)$_9$CH_3), 20.9 (Ar–O(CH_2)$_8$-CH_2CH_3), 23.0 (Ar–O(CH_2)$_7$CH_2CH_2CH_3), 27.1 (Ar–O(CH_2)$_6$CH_2(CH_2)$_2$CH_3), 27.8 (Ar–O(CH_2)$_5$CH_2(CH_2)$_3$CH_3), 28.9 (Ar–O(CH_2)$_4$CH_2(CH_2)$_4$CH_3), 29.3 (Ar–O(CH_2)$_3$-CH_2(CH_2)$_5$CH_3), 29.9 (Ar–O(CH_2)$_2$CH_2(CH_2)$_6$CH_3), 30.1 (Ar–OCH_2CH_2(CH_2)$_7$CH_3), 30.6, 31.3 (Ar–CH_2–Ar), 39.7 (Ar–CH_2–COOH), 76.4 (Ar–OCH_2(CH_2)$_8$CH_3), 125.3, 126.4, 127.1, 128.2, 128.6, 129.5, 134.3 (Ar), 148.5, 149.7 (Ar*C*–OH), 151.6 (Ar*C*–O(CH_2)$_9$CH_3) and 172.5 (Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z = 739.2 $[M + H]^+$, 761.3 $[M + Na]^+$ and 737.2 $[M - H]^-$.

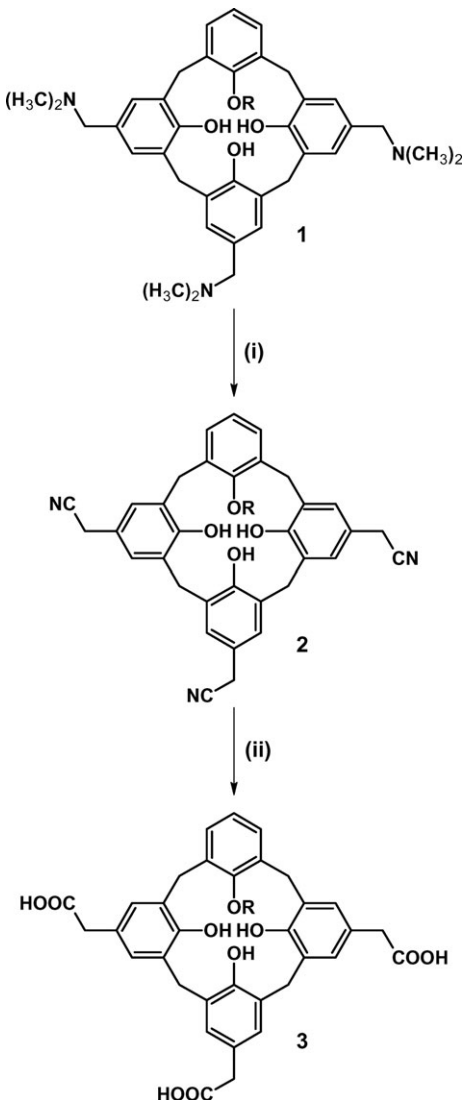
5,11,17-Tris[(carboxy)methyl]-25-monododecoxy-26,27,28-trihydroxycalix[4]arene (3k). Yield 85%, creamy solid, mp = 152 °C. IR: ν = 3180 (O–H), 2930 (C–H), 1700 (C=O), 1600 (C=C), 1460 (C–H) and 1080 (C–O) cm^{-1}. ^1H NMR (DMSO): δ 0.83 (t, 3H, $^3J_{H-H}$ = 6.1 Hz, Ar–O(CH_2)$_{11}$CH_3), 1.23 (m, 6H, Ar–O(CH_2)$_8$CH_2CH_2CH_2CH_3), 1.30 (m, 4H, Ar–O(CH_2)$_6$CH_2CH_2(CH_2)$_3$CH_3), 1.34 (m, 4H, Ar–O(CH_2)$_4$-CH_2CH_2(CH_2)$_5$CH_3), 1.44 (m, 2H, Ar–O(CH_2)$_3$CH_2(CH_2)$_7$-CH_3), 1.65 (m, 2H, Ar–O(CH_2)$_2$CH_2(CH_2)$_8$CH_3), 1.99 (m, 2H, Ar–OCH_2CH_2(CH_2)$_9$CH_3), 3.24 (s, 6H, Ar–CH_2–COOH), 3.44 (d, 2H, $^2J_{H-H}$ = 13.5 Hz, Ar–CH_2–Ar), 3.50 (d, 2H, $^2J_{H-H}$ = 13.5 Hz, Ar–CH_2–Ar), 4.00 (t, 2H, $^3J_{H-H}$ = 6.4 Hz, Ar–OCH_2(CH_2)$_{10}$CH_3), 4.20 (d, 2H, $^2J_{H-H}$ = 13.5 Hz, Ar–CH_2–Ar), 4.24 (d, 2H, $^2J_{H-H}$ = 13.5 Hz, Ar–CH_2–Ar), 6.83–7.15 (m, 9H, Ar–*H*), 8.91 (s, 2H, Ar–O*H*) and 9.53 (s, 1H, Ar–O*H*). ^{13}C NMR (DMSO): δ 13.1 (Ar–O(CH_2)$_{11}$CH_3), 20.7 (Ar–O(CH_2)$_{10}$CH_2CH_3), 22.8 (Ar–O(CH_2)$_9$CH_2CH_2-CH_3), 26.9 (Ar–O(CH_2)$_8$CH_2(CH_2)$_2$CH_3), 27.3 (Ar–O(CH_2)$_7$-CH_2(CH_2)$_3$CH_3), 27.9 (Ar–O(CH_2)$_6$CH_2(CH_2)$_4$CH_3), 28.7 (Ar–O(CH_2)$_5$CH_2(CH_2)$_5$CH_3), 29.1 (Ar–O(CH_2)$_4$CH_2(CH_2)$_6$-CH_3), 29.7 (Ar–O(CH_2)$_3$CH_2(CH_2)$_7$CH_3), 29.9 (Ar–O(CH_2)$_2$-CH_2(CH_2)$_8$CH_3), 30.1 (Ar–OCH_2CH_2(CH_2)$_9$CH_3), 30.6, 31.5 (Ar–CH_2–Ar), 39.6 (Ar–CH_2–COOH), 76.4 (Ar–OCH_2-(CH_2)$_{10}$CH_3), 125.2, 126.3, 127.1, 128.4, 128.8, 129.2, 134.4 (Ar), 148.9, 149.6 (Ar*C*–OH), 151.3 (Ar*C*–O(CH_2)$_{11}$CH_3) and 172.6 (Ar–CH_2–*C*OOH). ES mass spectrum (DMSO): m/z = 766.6 $[M + H]^+$, 789.5 $[M + Na]^+$, 805.4 $[M + K]^+$ and 765.2 $[M - H]^-$.

Results and discussion

Synthesis

The tris[*para*-(dimethylamino)methyl]trihydroxy-mono-*O*-alkyl-calix[4]arenes, **1a–k**, were synthesised by following described procedures.[20] The synthetic route used is given in Scheme 1. The reactions of **1a–k** with methyl iodide in DMSO produced the corresponding quaternary ammonium salts, and nucleophilic attack with excess sodium cyanide yielded tris[*para*-(cyano)methyl]-trihydroxy-mono-*O*-alkyl-calix[4]arenes **2a–k** in good yields.[23]

The tris[(carboxy)methyl]trihydroxy-mono-*O*-alkyl-calix[4]arenes, **3a–3k**, were prepared by the hydrolysis of **2a–k** in alcoholic potassium hydroxide after neutralisation with HCl, and were isolated in good yields. The structures of these products were confirmed by IR, ^1H NMR, ^{13}C NMR and ES mass spectrometry analysis.



Scheme 1 The synthetic route to compounds **3a–3k**. R: a = CH_3, b = C_2H_5, c = C_3H_7, d = C_4H_9, e = C_5H_{11}, f = C_6H_{13}, g = C_7H_{15}, h = C_8H_{17}, i = C_9H_{19}, j = $C_{10}H_{21}$ and k = $C_{12}H_{25}$. (i) CH_3I, DMSO 30 min, NaCN, reflux 3 h, (ii) KOH/EtOH/H_2O, reflux 72 h.

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The IR spectra of **2a–k** showed a medium to strong absorption between 2248 and 2250 cm^{-1}, indicating the presence of organic CN stretching bands.

The ^1H NMR spectrum of **2a** showed two doublets at δ 3.37 and 3.49 (^2J = 13.0 Hz) for the equatorial protons, and two doublets at δ 4.24 and 4.35 (^2J = 13.0 Hz) for the axial protons of the bridging methylene groups. In the case of **2b**, the bridging methylene protons were present as one doublet at δ 3.48 (^2J = 13.1 Hz) for the equatorial protons and one doublet at δ 4.30 (^2J = 13.1 Hz) for the axial protons. Compounds **2c–k** showed two pairs of doublets for the methylene protons at δ 4.15–4.30 for the axial protons and δ 3.35–3.50 for the equatorial protons. As $\Delta\delta$ between the signals arising from the axial and equatorial protons is greater than 0.8 ppm, the conformations of the compounds were assigned as cones.[24]

For **2a**, a characteristic singlet at δ 4.15 corresponds to the signal of the methyl ether group, and for **2b**, a characteristic quartet at δ 4.28 corresponds to the signal of the methylene of the ethyl ether group; however, for **2c–k**, ^1H NMR showed one triplet for the ether group (O–CH_2) protons in the region between δ 4.11 and 4.17.

For all of the compounds, a characteristic singlet in the region of δ 3.55 arose from the Ar–CH_2–CN protons.

The protons of phenolic hydroxyl groups were observed as one singlet in the region of δ 9.4 (2H) and a second singlet in the region of δ 9.7 (1H).

The ^{13}C NMR spectrum of **2a** presented signals between δ 31.0 and 31.5 corresponding to the methylene bridges; a signal at δ 63.4 was assigned to the methyl ether group and a signal at δ 117.9 was assigned to the carbon atoms of the nitrile groups. The ^{13}C NMR spectra of **2b–k** showed signals between δ 31.3 and 31.9 for the methylene bridges, a signal at δ ~73 for the methylene ether groups and a signal at δ ~118 for the carbon atoms of the nitrile groups.

For the series **3a–3k**, the structures of these compounds were confirmed by mass spectrometry, and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

The infrared spectra of **3a–3k** showed the disappearance of the signal between 2248 and 2250 cm^{-1}, the presence of a C=O stretching mode at 1700 cm^{-1}, and broad OH stretching modes between 3160 and 3180 cm^{-1}, characteristic of carboxylic acids.

In DMSO-d_6 solution, the ^1H NMR spectrum of **3a** showed a singlet (6H) at δ 3.31 (Ar–CH_2–COOH), two doublets at δ 3.39 and δ 3.48 ($^2J_{H-H}$ = 13.4 Hz) for the equatorial protons, and two doublets at δ 4.18 and 4.25 ($^2J_{H-H}$ = 13.4 Hz) for the axial protons of the bridging methylene groups. This again shows the compound to be present in the cone conformation.

A singlet at δ 4.01 (3H) corresponding to the methyl ether group, a multiplet at δ 6.95–7.15 (9H) for the aromatic protons, two singlets at δ 8.80 (2H) and δ 9.50 (1H) corresponding to the phenolic hydroxyl protons, and a singlet at δ 12.18 (3H) of the carboxylic acid were observed.

The $^{13}C\{^1H\}$ NMR spectrum of **3a** showed signals at δ 30.4 and 30.9 for the methylene bridge carbon atoms, showing that the molecule is present in the cone conformation. One signal was observed at δ 39.6 for the Ar–CH_2–COOH carbon, one peak at δ 63.6 for the methoxy carbon atom and a peak at δ 172.9 for the carboxylic acid carbon.

Similarly, the ^1H NMR spectra of **3b–k** showed two pairs of two doublets (8H) for the Ar–CH_2–Ar protons, a singlet (6H) for the Ar–CH_2–COOH group, a triplet for the ether group (O–CH_2), a multiplet between δ 6.84 and 7.19 (9H) for the aromatic protons, two singlets of intensity 2H and 1H, respectively, which were assigned to the phenolic protons, and a singlet (3H) for the carboxylic acid protons. The ^{13}C NMR spectra of **3b–k** confirmed the cone conformation, showing two peaks for the bridging methylene carbons in the region of δ ~30, one peak for the methylene carbon alpha to the ether group at δ ~76 and one peak for the carboxylic acid carbon group at δ ~172.

Solid-state structural studies

Crystals of compounds **2b**, **2d**, **2e** and **2f** were obtained by the slow diffusion of methanol into acetonitrile solutions of these compounds.‡

For compound **2b**, the molecular structure (Fig. 1) shows that there is inclusion of an acetonitrile molecule into the macrocyclic cavity, thus the presence of three methylene functions at the *para*-position does not remove the inclusion capacity of the calix[4]arene. This can be compared to the situations for *para*-sulfonatomethyl-calix[4]arene[21] and *para*-hexyl-calix[4]arene,[22] where all four *para*-positions carry methylene groups, and for which steric hindrance blocks inclusion. There are short contacts between the methyl group inserted into the cavity and the centroids of the three unsubstituted aromatic

‡ Crystal data for **2b**: $C_{38}H_{34}N_4O_4$, M = 610.69, dark yellow prism, 0.30 × 0.20 × 0.10 mm, triclinic, space group $P\bar{1}$ (no. 2), a = 11.3123(4), b = 11.9398(5), c = 12.7159(4) Å, α = 72.295(2), β = 83.791(2), γ = 74.991(2)°, V = 1579.5(1) Å^3, Z = 2, D_c = 1.284 g cm^{-3}, F_{000} = 644, KappaApexII, MoK$_\alpha$ radiation, λ = 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 47.1°, 20 536 reflections collected, 4685 unique (R_{int} = 0.065). Final GooF = 1.03, R = 0.050, wR = 0.109, R indices based on 3641 reflections with $I > 2\sigma(I)$ (refinement on F^2), 421 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.084 mm^{-1}. CCDC 697244.†

Crystal data for **2d**: $C_{38}H_{35}N_3O_4$, M = 597.69, colourless block, 0.25 × 0.20 × 0.15 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 9.6286(3), b = 19.9708(7), c = 15.8164(4) Å, β = 92.258(2)°, V = 3039.0(2) Å^3, Z = 4, D_c = 1.306 g cm^{-3}, F_{000} = 1264, KappaApexII, MoK$_\alpha$ radiation, λ = 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 55.0°, 25 157 reflections collected, 6937 unique (R_{int} = 0.073). Final GooF = 1.04, R = 0.079, wR = 0.150, R indices based on 4389 reflections with $I > 2\sigma(I)$ (refinement on F^2), 410 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.085 mm^{-1}. CCDC 697245.†

Crystal data for **2e**: $C_{39}H_{38}N_3O_{4.50}$, M = 620.72, colourless block, 0.30 × 0.30 × 0.10 mm, orthorhombic, space group $P2_12_12$ (no. 18), a = 17.6804(2), b = 18.0029(4), c = 10.2337(4) Å, V = 3257.4(2) Å^3, Z = 4, D_c = 1.264 g cm^{-3}, F_{000} = 1316, KappaApexII, MoK$_\alpha$ radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 54.9°, 48 183 reflections collected, 7416 unique (R_{int} = 0.074). Final GooF = 1.03, R = 0.085, wR = 0.210, R indices based on 5345 reflections with $I > 2\sigma(I)$ (refinement on F^2), 421 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.083 mm^{-1}. CCDC 693571.†

Crystal data for **2f**: $C_{40}H_{39}N_3O_4$, M = 625.74, colourless block, 0.35 × 0.25 × 0.25 mm, orthorhombic, space group $P2_12_12$ (no. 18), a = 17.6752(5), b = 17.6984(7), c = 10.6227(4) Å, V = 3323.0(2) Å^3, Z = 4, D_c = 1.251 g cm^{-3}, F_{000} = 1328, KappaApexII, MoK$_\alpha$ radiation, λ = 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 52.8°, 38 743 reflections collected, 6792 unique (R_{int} = 0.109). Final GooF = 1.07, R = 0.093, wR = 0.222, R indices based on 4705 reflections with $I > 2\sigma(I)$ (refinement on F^2), 428 parameters, 3 restraints. Lp and absorption corrections applied, μ = 0.081 mm^{-1}. CCDC 693572.†

All structures were solved and refined using the programs SHELXS-97[29] and SHELXL-97,[30] respectively.

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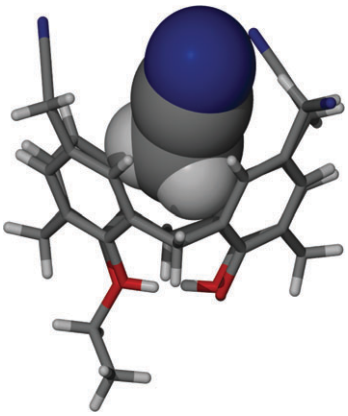

Fig. 1 The molecular structure of the acetonitrile inclusion complex of **2b**.

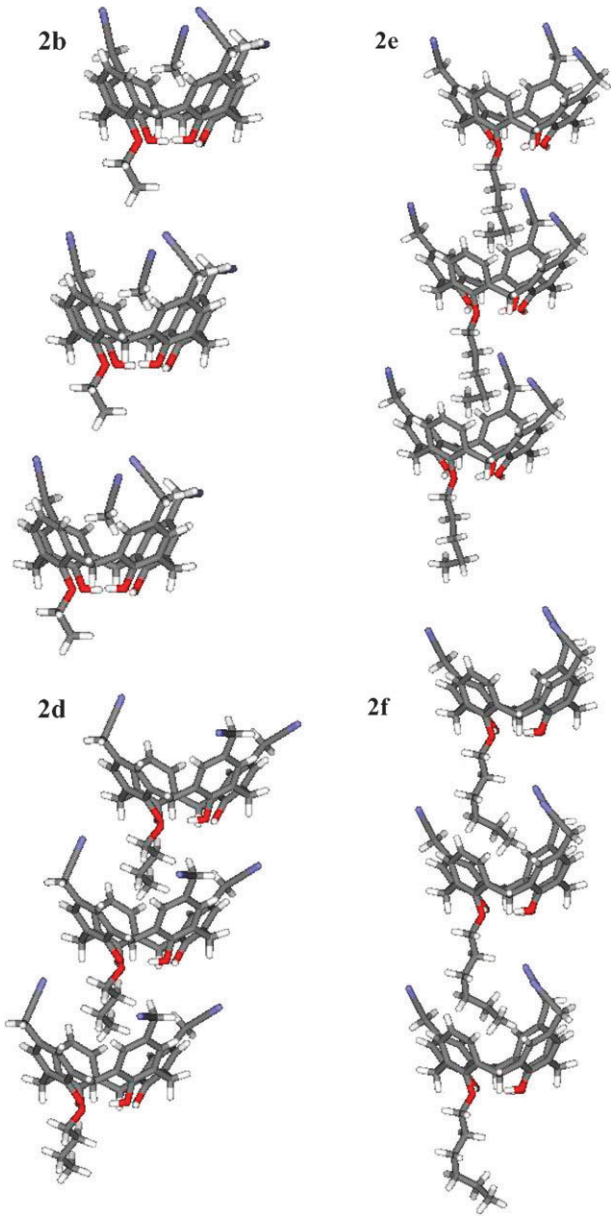

Fig. 2 Inclusion polymers for **2b**, **2d**, **2e** and **2f**.

rings (3.53, 3.61 and 3.68 Å), with a somewhat longer distance to the centroid of the substituted ring (3.88 Å).

The compounds pack as true 1-D inclusion polymers for **2d**, **2e** and **2f**, and as a pseudo 1-D inclusion polymer for **2b**, as shown in Fig. 2,.

The short contacts between the carbon atoms of the included chains and the aromatic rings are given in Tables 1–6. The distances between the stacked molecules, measured from the methylene carbon atoms at the *para*-position and the phenolic oxygen atoms, are 7.191(4) Å for **2b**, 5.813(4) Å for **2d**, 5.668(6) Å for **2e** and 6.021(7) Å for **2f**.

The differences in orientation of the nitrile and aliphatic groups are shown in Fig. 3.

Effectively, there is almost perfect superposition of the alkyl chains for all compounds except **2d**; this is also apparent in the alignment of the calix[4]arene macrocycles in the 1-D inclusion polymer. For **2d**, the alkyl chain is oriented away from the molecular axis, while for the other compounds, the alkyl chain is oriented along the axis (Table 7).

The torsion angles for the orientation of the nitrile groups with respect to the aromatic rings are given in Table 8; again

Table 1 Hydrogen bonds and C···π interactions in the solid-state for **2b**

D–H···A	*d*(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	∠(D–H···A)(°)
O2–H2···O3	0.84	1.87	2.689(2)	163
O3–H3···O4	0.84	1.89	2.724(2)	171
O4–H4···O1	0.84	1.87	2.708(2)	172
C24–H24···N3[a]	0.95	2.59	3.498(4)	159
C33–H33B···N2[b]	0.99	2.54	3.421(4)	148
C37–H37C···π3	0.98	2.64	3.538(4)	153

[a] $-x, -y + 2, -z$. [b] $x, y, z - 1$.

Table 2 π···π interactions in the solid-state for **2b**

Rings	D(π···π)/Å
π3···π3[a]	3.33

[a] $1 - x, 1 - y, 1 - z$.

Table 3 Hydrogen bonds and C···π interactions in the solid-state for **2d**

D–H···A	*d*(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	∠(D–H···A)(°)
O2–H2···O1	0.84	1.91	2.736(3)	166
O3–H3A···O2	0.84	1.85	2.679(3)	168
O4–H4A···O3	0.84	1.80	2.616(3)	163
C12–H12···N3[a]	0.95	2.62	3.454(4)	147
C31–H31A···O1[b]	0.99	2.52	3.442(4)	155
C35–H35A···N3[c]	0.99	2.59	3.377(4)	136
C35–H35B···N1[d]	0.99	2.60	3.523(4)	155
C38–H38B···π1[e]	0.98	2.76	3.583(5)	123
C37–H37A···π2[e]	0.99	3.01	3.817(4)	125
C37–H37A···π3[e]	0.99	2.99	3.808(4)	125
C38–H38A···π4[e]	0.98	2.95	3.759(5)	124

[a] $-1 + x, y, z$. [b] $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$. [c] $1 + x, y, z$. [d] $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$. [e] $-1 + x, y, z$.

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Table 4 π···π interactions in the solid-state for **2d**

Rings	$d(\pi\cdots\pi)$/Å
π2···π4[a]	3.355
π3···π3[b]	3.411

[a] $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$. [b] $2-x, -y, 1-z$.

Table 5 Hydrogen bonds and C···π interactions in the solid-state for **2e**[a]

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠(D–H···A) (°)
O2–H2···O1	0.84	2.05	2.765(4)	143
O3–H3A···O2	0.84	2.19	2.725(4)	121
O4–H4A···O3	0.84	1.98	2.673(4)	139
C31–H31A···N1[b]	0.99	2.38	3.341(7)	165
C38–H38B···π4[c]	0.99	2.99	3.82(1)	123
C39–H39B···π2[c]	0.98	3.10	3.76(1)	137

[a] π···π stacking distance along a = 3.38 Å. [b] $-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$. [c] $x, y, 1+z$.

Table 6 Hydrogen bonds and C···π interactions in the solid-state for **2f**[a]

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠(D–H···A) (°)
O2–H2···O1	0.84	1.93	2.757(5)	168
O3–H3A···O2	0.84	1.87	2.684(5)	164
O4–H4A···O1	0.84	2.01	2.836(5)	167
C19–H19···N1[b]	0.95	2.61	3.458(7)	149
C31–H31B···N3[c]	0.99	2.38	3.371(9)	176
C39–H39A···N2[d]	0.99	2.59	3.58(2)	173
C40–H40C···π1[e]	0.98	2.80	3.70(2)	113
C40–H40B···π3[e]	0.98	2.76	3.69(2)	101

[a] π···π stacking distance along a = 3.38 Å. [b] $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$. [c] $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$. [d] $x, y, 1+z$. [e] $x, y, -1+z$.

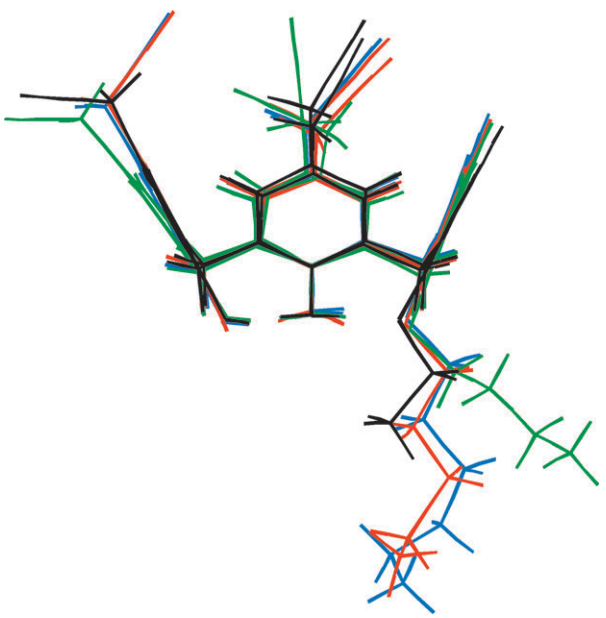

Fig. 3 Superposition of the four calixarene molecules: black **2b**, green **2d**, red **2e** and blue **2f**.

Table 7 The orientation of the macrocycle plane[a] relative to the axis of the 1-D polymer of **2b**, **2d**, **2e** and **2f**

Structure	Angle (°)
2b	13.4(2)
2d	38.8(2)
2e	12.9(3)
2f	11.1(4)

[a] Defined by the four CH_2 groups of the macrocyclic ring.

Table 8 Torsion angles between the nitrile groups and the aromatic rings in the calixarenes

Structure	Torsion angle (°)		
2b	−61.2(3)	54.5(3)	60.1(3)
2d	−88.1(4)	−30.4(4)	−0.4(5)
2e	46.2(6)	88.0(6)	−45.6(6)
2f	44.4(7)	86.7(7)	−50.2(8)

for compound **2d** there is a difference in the orientations with one torsion of 0° where the other compounds show torsion angles of 60°, −45° and −50° for the corresponding group.

The packing diagrams along the b axis for **2b**, a axis for **2d** and c axis for **2e** are given in Fig. 4a, b and c, respectively.

In all of the structures, intermolecular π–π aromatic interactions, in the range of 3.3–4 Å along a single axis, serve to enhance the packing cohesion (see Table 2 and Table 4).

Aqueous self-assembly

Critical micelle concentrations (CMCs) were determined from the concentration-dependent variation of the surface pressure, measured using a microtensiometer equipped with a stainless steel needle probe.

Compounds **3a–3k** all formed micelles in aqueous media at pH values of 6 and 8. Typical CMC isotherms are shown in Fig. 5 and Fig. 6, for **3a**, **3d**, **3g** and **3k**, at pH values of 6 and 8, respectively. The CMC data are summarised in Table 9 and Table 10. At pH values of 5.5 and lower, precipitation occurred; undoubtedly this arose from re-protonation of the carboxylate head group and the resultant formation of intra- and intermolecular hydrogen-bonded supramolecular polymers.

At the biologically relevant pH values of 6 and 8, all of the compounds showed typical behaviour in the formation of micelles. The CMC value observed for **3k**, with a chain length of 12 carbon atoms, is analogous to that observed for dodecylmaltoside (DDM), a detergent that is widely used for membrane extractions and which has the same number of carbon atoms in the hydrophobic chain.[25]

In contrast to the analogous tris[(dimethylamino)methyl]-25-monoalkoxy-26,27,28-trihydroxycalix[4]arene derivatives, there is a clear relation between the length of the alkyl chain, and both the CMC and the observed surface tension at the CMC. This is illustrated in Fig. 7 and Fig. 8. The difference between the two groups of molecules arises from the much lower hydrophilicity of the alkyl-*N*,*N*-dimethyl ammonium head groups in the case of the tris[(dimethylamino)methyl]-25-monoalkoxy-26,27,28-trihydroxycalix[4]arene derivatives, as compared to the carboxylate anion head groups in the

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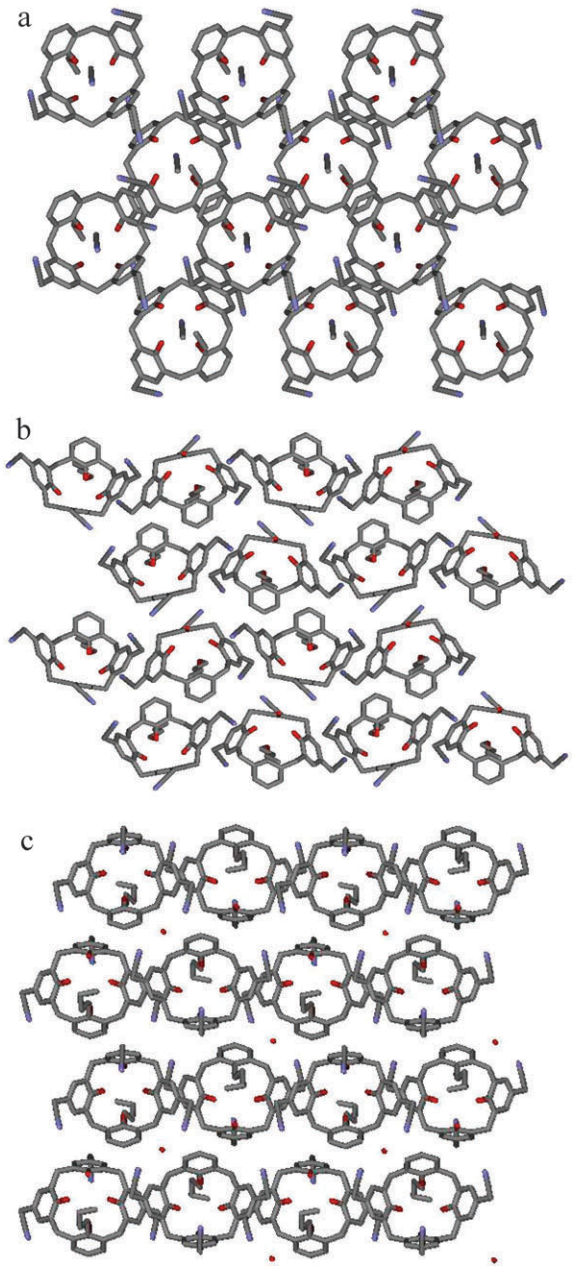

Fig. 4 Packing diagrams: (a) **2b** along the b axis; (b) **2d** along the a axis; (c) **2e** along the c axis.

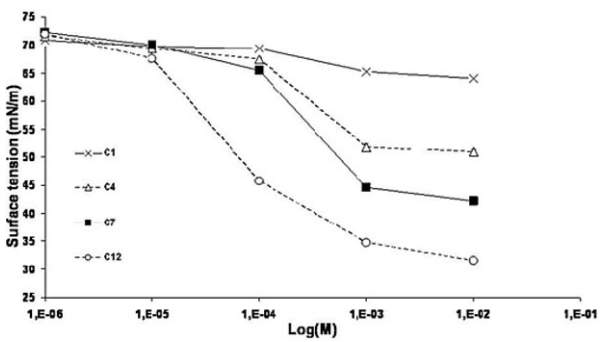

Fig. 5 Surface tension *vs.* concentration isotherms for **3a**, **3d**, **3g** and **3k** at pH 6.

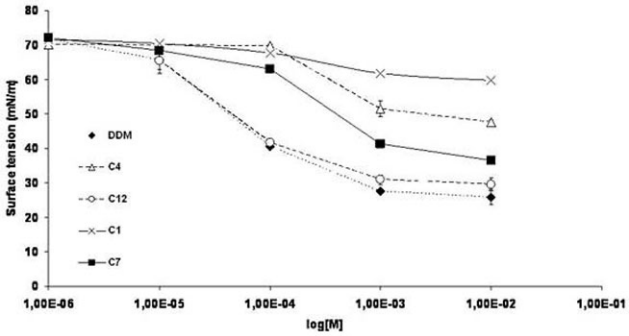

Fig. 6 Surface tension *vs.* concentration isotherms for **3a**, **3d**, **3g** and **3k** at pH 8. For comparison, the isotherm for dodecylmaltoside (DDM), a commonly used detergent, is given.

Table 9 Surface tension and CMC data for compounds **3a–3k** at pH 6

Chain length	1	2	3	4	5	6	7	8	9	10	12
CMC/10^{-3} M	1.0	1.6	1.3	1.2	1.3	1.2	1.2	1.2	0.1	0.5	0.1
Surface pressure/mN m^{-1}	60	58	44	48	41	40	36	38	31	34	39

Table 10 Surface tension and CMC data for compounds **3a–k** at pH 8

Chain length	1	2	3	4	5	6	7	8	9	10	12
CMC/10^{-3} M	1.3	1.3	1.0	1.1	1.2	1.0	1.1	0.2	0.4	0.1	0.1
Surface pressure/mN m^{-1}	64	60	47	51	45	48	42	44	39	39	32

current study. As noted above, even partial protonation of the carboxylate groups led to aggregation and precipitation.

With regards to the CMC, for chain lengths between one and seven carbon atoms at pH 6, and one and eight carbon atoms at pH 8, the CMC values are effectively constant at around 1 mM at pH 6 and around 1.3 mM at pH 8. For the longer chain lengths, the CMC values are also roughly constant at around 0.1 mM, values that are similar to that of DDM. Thus, there is a clear break in the CMC that is dictated by the chain length.

For the surface tension values, there is a decrease from 65 mN m^{-1} for **3a** to 32 mN m^{-1} for **3k** at pH 6, and from 60 mN m^{-1} for **3a** to 30 mN m^{-1} for **3k** at pH 8;[25] again, the

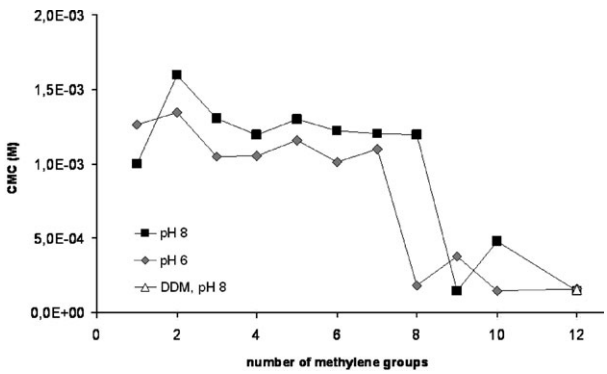

Fig. 7 CMC values for compounds **3a–k** as a function of chain length at pH values of 6 and 8. For comparison, the value for DDM at pH 8 is given.

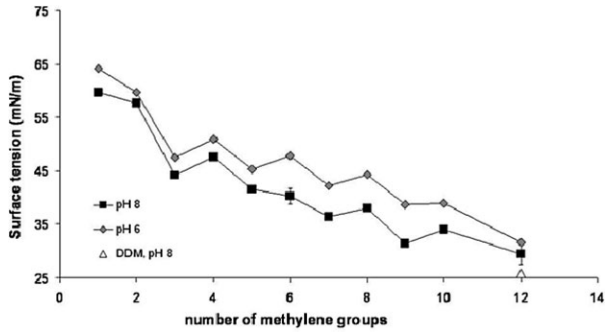

Fig. 8 Surface tension at the CMC for compounds **3a–k** as a function of chain length at pH values of 6 and 8. For comparison, the value for DDM at pH 8 is given.

values observed for **3k** are similar to those of DDM. More interestingly, there is clearly an odd–even effect, well known for self-assembled monolayers,[26] and for the effects monolayers of long chain (C16–C32) alkyl alcohols have on the freezing point of water.[27] Such effects are known to arise from the orientation of the terminal carbon atom with regards to the interface.

The odd–even effect has been observed for the micellisation of Gemini surfactants, where it was ascribed to the differences in the hydrophobic aggregation behaviour of the alkyl chains.[28] However, the authors observed that the odd–even effect only appeared for chain lengths longer than eight carbon atoms. Interestingly, in the current work, the odd–even effect is clearly observed for chain lengths of three carbon atoms or longer. It would seem probable that the variation in the orientation of the terminal methyl group, as clearly seen in Fig. 2, with regards to the macrocyclic axis of the calix[4]arene head group is dominant in the case of the current molecules.

Conclusion

In conclusion, a series of novel trianionic surfactants based on monosubstituted calix[4]arenes, with systematic variation in the hydrophobic alkyl chain length between one and twelve carbon atoms, has been synthesised. All of the surfactant molecules displayed aggregation behaviour that is typical of micelle formation. The surface activity behaviour varied as a function of chain length, showing a clear difference in CMC values between short and long alkyl chains that was pH dependent. With the surface tension measurements, a clear odd–even effect was seen.

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