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Anion receptors based on ureido-substituted thiacalix[4]arenes and calix[4]arenes

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ABSTRACT

The regioselective nitration of 25,27-dipropoxythiacalix[4]arene was carried out as a key step in the synthesis of thiacalix[4]arene derivative bearing two arylureido functions on the upper rim. The pre-organisation of ureido units using the thiacalix[4]arene/calix[4]arene moieties as a molecular scaffold gave novel anion receptors. These compounds, albeit based on hydrogen bonding interactions, show good complexation ability even in highly HB-competitive solvent, such as DMSO. Direct comparison of otherwise identical structures **6a** and **7a** revealed remarkable dominance of the thiacalix[4]arene derivative over its classical analogue in anion binding.

1. Introduction

The chemistry of thiacalixarenes, more than a decade since their first appearance,[1] still does not fully meet expectations. Despite their very interesting complexation and molecular recognition abilities,[2] thiacalixarenes are only seldom used in the design of more elaborate receptors and host molecules. Not surprisingly, the introduction of four sulfur atoms imparts many novel features if compared with the chemistry of classical calixarenes[3] possessing methylene bridges. As a result, the broader application of thiacalixarenes in supramolecular chemistry is still limited by fragmentary knowledge of their chemistry and the absence of general derivatization methods, otherwise well established for $-CH_2-$ analogues. Hence, a deeper understanding of their derivatisation could make thiacalixarenes very useful building blocks for the design of novel receptors.

Nitro-substituted calix[4]arenes act as common intermediates for the preparation of amino-substituted derivatives (via reduction). Accordingly, the nitration of classical calix[4]arenes is a well-established reaction that can be carried out either directly[4] or via the *ipso*-substitution[5] procedure. On the other hand, the nitration in thiacalix[4]arene series is not so easy, since the oxidation of sulfur bridges can occur as a competitive reaction.[6] As we have shown, this weak point can be circumvented using thiacalixarene with pre-oxidised bridges (sulfones).[7] The preparation of tetranitrothiacalix[4]arene was described recently using direct[8] nitration. Unfortunately, the tetranitro derivative is very insoluble in common organic solvents, which makes subsequent shaping of the molecule (alkylation/acylation on the lower rim) difficult, and in fact, no such procedure has been reported so far.

Anion complexation has been recognised as an important part of supramolecular chemistry as documented by numerous reviews and books published recently.[9] Among them the calixarene-based receptors for anion recognition represent a well-established research topic.[10] The introduction of urea moieties onto the calixarene skeleton enables the construction of neutral well-preorganised anion receptors designed for complexation via directional hydrogen bonding from the urea functions.[11] During our ongoing research into anion recognition[12] we have attempted the synthesis of similar receptors based on thiacalixarenes to demonstrate the usefulness of this novel system. In this paper, we report the synthesis and complexation behaviour of the first anion receptor based on upper-rim substituted thiacalix[4]arene.

2. Results and discussion

While the alkylation of classical calix[4]arene gives distally dialkylated compounds always in the *cone* conformation,[3] two separable conformers can be isolated in the case of thiacalix[4]arene.[13] Thus, dialkylation of **1** with propyl iodide in MeCN gave a mixture of *cone* **2** and *1,2-alternate* **2a′** (Scheme 1) where both conformers can be obtained by column chromatography on silica gel in 53% and 15% yields, respectively. During our ongoing research on the thiacalixarene series, we wondered if these isomers can be used for the subsequent regioselective derivatisation of thiacalixarenes without mutual interconversion.[14] In the case of compound

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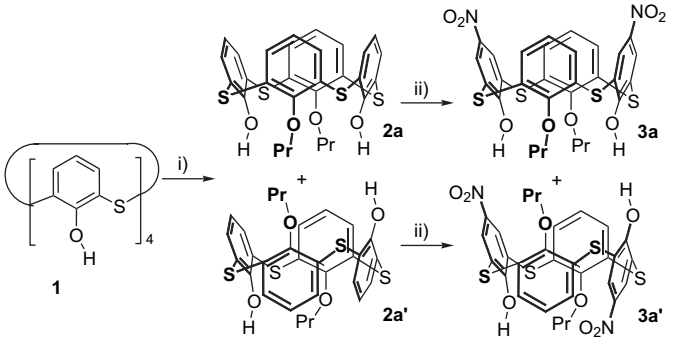
2a the best result was achieved using concd HNO_3 in acetic acid/$CHCl_3$ mixture. After 3 h reflux under these conditions the dinitro derivative **3a** (*cone*) was isolated in 68% yield as the main product. The corresponding *1,2-alternate* conformation **3a**′ was obtained similarly starting from **2a**′, albeit in lower yield (44%). As both nitro derivatives **3a** and **3a**′ are stable under common conditions they can be used independently for further synthesis.



Scheme 1. (i) K_2CO_3/*n*-PrI/MeCN, reflux, 7 days (**2a**, 53%; **2a**′, 15%); (ii) 65% HNO_3/$CHCl_3$–AcOH, reflux, 3 h (**3a**, 68%; **3a**′, 44%).

The structures of the novel nitro derivatives were confirmed by ^{1}H NMR analysis. Thus, compound **3a** possesses one singlet of nitro-substituted phenyl ring (δ 8.57 ppm), doublet and triplet due to the unsubstituted ring (δ 7.20 and 6.74 ppm) with typical interaction constant (J=7.7 Hz) in the aromatic part of spectrum. The theoretically possible *1,3-alternate* conformation (having the same splitting pattern) was excluded by NOE experiments. Surprisingly, the splitting pattern of the *1,2-alternate* conformer **3a**′ is identical to that of **3a** (e.g., only one singlet for nitro-substituted ring at δ 8.40 ppm) and does not correspond to the expected spectrum of *1,2-alternate*. This phenomenon was recently observed in distally disubstituted thiacalixarenes[9] and it is consistent with fast exchange between two *1,2-alternate* conformations.

The final evidence for the structure of **3a**′ was obtained by single crystal X-ray diffraction analysis (suitable monocrystals were obtained by slow evaporation of an EtOAc/CH_2Cl_2 solution). The molecule adopts a *1,2-alternate* conformation with two nitro groups pointing to the opposite sides of the molecule (Fig. 1a). A rather unusual structural motif was found in the crystal packing of **3a**′ (Fig. 1b). The neighbour molecules are interconnected by hydrogen bonding interactions between the oxygen atom of nitro group and *meta*-hydrogen of the corresponding phenolic units (O···H distance=2.54 Å).

Calixarenes bearing ureido functions on the upper rim are known as anion receptors acting through hydrogen bonding interactions.[10–12] Hence, compound **3a** immobilised in the *cone* conformation was chosen for the synthesis of thiacalixarene-based anionic receptor bearing two ureido moieties. The corresponding reaction pathway is depicted in Scheme 2. Dinitro derivative **3a** was reduced using $SnCl_2$ in refluxing ethanol to give amino-substituted thiacalixarene **4a**, which was subsequently condensed with *p*-tolyl isocyanate. The resulting receptor **6a** was isolated in 40% yield. To compare the influence of the thiacalix[4]arene skeleton on a binding process, the corresponding derivatives of classical calix[4]arene **7a** and **7b** were prepared using a similar synthetic strategy.

The complexation ability of derivatives **6a** and **7a**,**b** towards selected anions (Cl^-, Br^-, acetate, benzoate) was measured by standard ^{1}H NMR titration experiments (DMSO-d_6) using a constant thiacalixarene concentration (0.1–2.0 mM) and increasing concentrations of the appropriate anion to obtain different host/guest ratios (0.1–40). All anions were used as tetrabutylammonium salts to avoid possible complexation of cationic species by the thiacalixarene cavity.

Despite the application of highly HB-competitive solvent, DMSO-d_6, the addition of corresponding anions to the solution of **6a** resulted in large down-field shifts of urea –NH– signals proving strong hydrogen bonding interactions with the anion. Thus, the originally almost unresolved –NH signals of free receptor **6a** (8.57 ppm) split into two resolved signals, which gradually moved

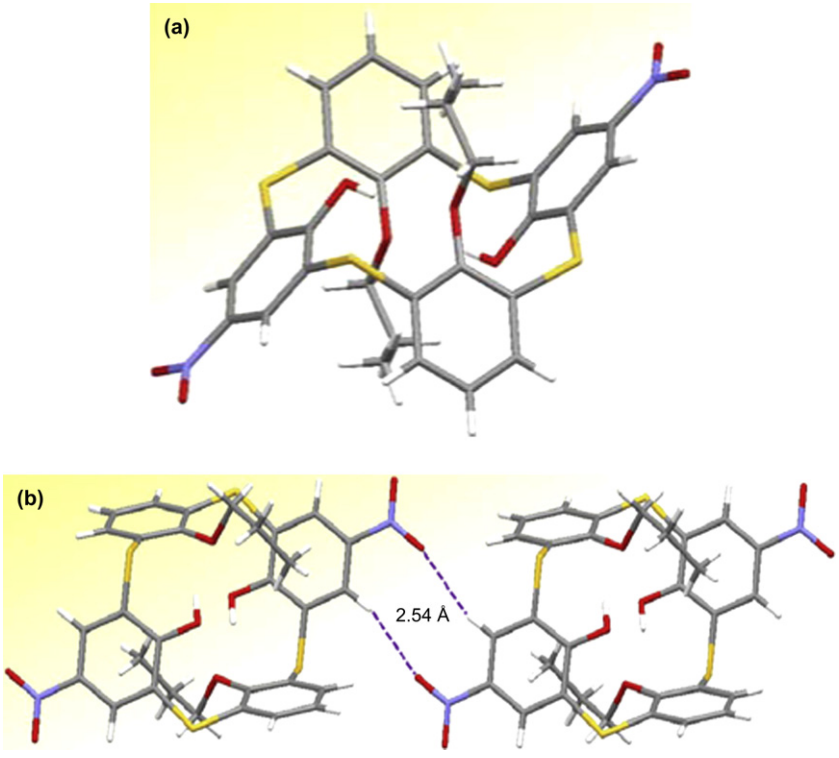
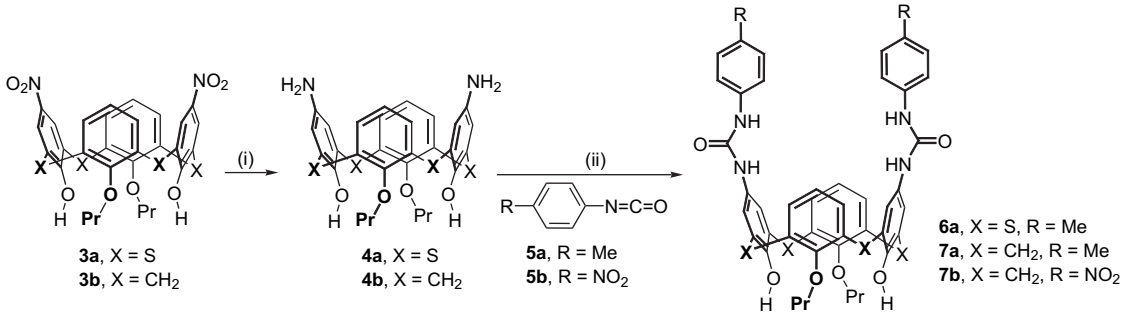


Figure 1. (a) X-ray structure of **3a**′, (b) hydrogen bonding interactions in the crystal packing of **3a**′.



Scheme 2. (i) $SnCl_2$/EtOH, reflux, overnight (**4a**, 49%); (ii) **4a** or **4b**+**5a**,**b**/CH_2Cl_2, rt, 4 days (**6a**, 40%; **7a**, 59%; **7b**, 38%).

up to 11.86 and 12.08 ppm (upon addition of 7 equiv of acetate). These unusually high complexation induced chemical shifts (ΔCIS=3.29 and 3.51) clearly indicate strong binding of the anion via cooperative hydrogen bonds (NH···Anion) operating simultaneously from both ureido fragments. The plot of induced chemical shifts (NH signals) versus anion concentration gave typical titration curves corresponding to the formation of 1:1 complexes (Fig. 2). The stoichiometry of complexation was further confirmed by Job plot analysis of selected systems. The corresponding complexation constants (Table 1) were calculated using an original non-linear regression curve-fitting program.[15]

As follows from Table 1, the complexation ability of **6a** towards halide anions is rather poor, and inversely proportional to halide's diameter (K_{Cl}=40 M^{-1} vs K_{Br}=5 M^{-1} vs K_I=0 M^{-1}). On the other hand, complexation of carboxylate anions is much stronger with preference for acetate ($K_{acetate}$=910 M^{-1}) over benzoate ($K_{benzoate}$=510 M^{-1}). The same trends can be seen for calix[4]arene derivatives **7a** and **7b**. Interestingly, direct comparison of otherwise identical structures **6a** and **7a** revealed remarkable dominance of thiacalix[4]arene derivative over its classical analogue in anion binding. As follows from Table 1, the corresponding complexation constants of thiacalixarene **6a** towards all selected anions are approximately doubled compared with those for classical calix[4]arene **7a** (e.g., K^{6a}=40 M^{-1} vs K^{7a}=24 M^{-1} for Cl^- or K^{6a}=510 M^{-1} vs K^{7a}=260 M^{-1} for benzoate). The possible explanation of this phenomenon could lie in the differences between the thiacalixarene and calixarene diameters where the bigger cavity of thiacalix[4]arene probably enables better cooperation of both ureido functions. Anyhow, the complexation data show interesting differences in behaviour of both systems, thus indicating the usefulness of the thiacalix[4]arene moiety as a promising building block in the design and construction of molecular receptors.

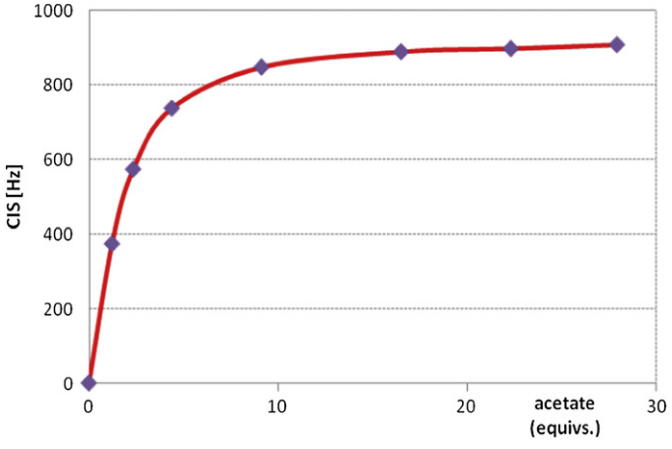


Figure 2. ^{1}H NMR titration curve for **6a** with $Bu_4N^+Ac^-$ (300 MHz, 298 K, DMSO-d_6).

Table 1
Binding constants K [M^{-1}][a] of receptors **6a** and **7a**,**b** towards selected anions[b]

Anion	6a	7a	7b
Cl^-	40±1.5	24±1.6	48±2.4
Br^-	4.6±0.5	3.6±0.8	5.0±1.2
$PhCOO^-$	510±110	260±35	1170±80
CH_3COO^-	910±180	430±40	2450±350

[a] ^{1}H NMR titration (300 MHz, DMSO-d_6, 298 K).
[b] All anions were used as tetra-*n*-butylammonium (Bu_4N^+) salts.

3. Conclusions

In conclusion, we have carried out the first regioselective nitration of 25,27-dipropoxythiacalix[4]arenes immobilised both in the *cone* and in the *1,2-alternate* conformations. Dinitro thiacalix[4]arene was transformed into diureido derivative, which shows remarkably better complexation ability towards selected anions if compared with the corresponding classical calix[4]arene analogue.

4. Experimental

4.1. General

Melting points were determined on a Boetius block (Carl Zeiss Jena, Germany) and are not corrected. The IR spectra were measured on an FT-IR spectrometer Nicolet 740 in $CHCl_3$ and/or in KBr. ^{1}H NMR spectra were recorded on a Varian Gemini 300 spectrometer. Dichloromethane used for the reaction was dried with CaH_2 and stored over molecular sieves. The purity of the substances and the courses of reactions were monitored by TLC using TLC aluminium sheets with Silica gel 60 F_{254} (Merck). Preparative TLC chromatography was carried out on 20×20 cm glass plates covered by Silica gel 60 GF_{254} (Merck).

Starting compound **3b**[5a] was prepared according to known procedure.

4.2. Synthesis of 5,17-dinitro-25,27-dipropoxy-thiacalix[4]arene-26,28-diol (*cone*) 3a

Thiacalixarene **2a** (460 mg, 0.687 mmol) was dissolved in 240 ml of $CHCl_3$, and a mixture of glacial acetic acid (5 ml) and 65% HNO_3 (3.9 ml) was then slowly added at room temperature to the solution. The reaction mixture was gradually warmed to reflux and stirring was continued for next 3 h at this temperature. The reaction mixture was then cooled down to room temperature and an aqueous $NaHCO_3$ (5% w/w) was added to neutralise the mixture. After separation, the organic layer was washed with water (3×100 ml) and dried over $MgSO_4$. After filtration the solvent was removed on vacuum evaporator and the remaining solid was reprecipitated from CH_2Cl_2/methanol mixture. The product **3a**

(360 mg, 68% yield) was obtained as orange solid after filtration. Mp: 309–311 °C (decomp.). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.76 (s, 2H, –OH), 8.57 (s, 4H, H-arom(NO_2)), 7.20 (d, 4H, J=7.6 Hz, *m*-H-arom), 6.74 (t, 2H, J=7.7 Hz, *p*-H-arom), 4.29 (t, 4H, J=6.6 Hz, –O–CH_2–), 2.08 (m, 4H, –OCH_2–CH_2–), 1.21 (t, 6H, J=7.3 Hz, –CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 163.9, 159.4, 139.5, 137.4, 132.1, 127.8, 125.9, 123.0, 79.7, 23.2, 10.5. IR (KBr) ν cm^{-1}: 3435, 2968, 1635, 1589, 1567, 1520, 1429, 1385, 1340, 1232. MS-ESI$^+$ *m*/*z* 670.0 [M]$^+$ (100%). Anal. Calcd for $C_{30}H_{26}N_2O_8S_4$: C, 53.72; H, 3.91; N, 4.18; S, 19.12%. Found: C, 53.60; H, 3.71; N, 4.11%.

4.3. Synthesis of 5,17-dinitro-25,27-dipropoxy-thiacalix[4]arene-26,28-diol (*1,2-alternate*) 3a′

This compound was prepared analogously to **3a** (see above) in 44% yield. Mp: 312–314 °C (decomp.). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.60 (s, 2H, OH), 8.40 (s, 4H, H-arom(NO_2)), 7.62 (d, 4H, J=7.7 Hz, *m*-H-arom), 7.10 (t, 2H, J=7.7 Hz, *p*-H-arom), 3.92 (t, 4H, J=6.6 Hz, –O–CH_2–), 1.40 (m, 4H, –OCH_2–CH_2–), 0.54 (t, 6H, J= 6.9 Hz, –CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 162.5, 158.8, 139.8, 136.3, 128.4, 127.1, 126.0, 121.8, 77.1, 22.5, 9.6. IR (KBr) ν cm^{-1}: 3436, 2966, 1589, 1563, 1517, 1429, 1383, 1336, 1253. Anal. Calcd for $C_{30}H_{26}N_2O_8S_4$: C, 53.72; H, 3.91; N, 4.18; S, 19.12%. Found: C, 53.35; H, 3.68; N, 4.03%.

4.4. Synthesis of 5,17-diamino-25,27-dipropoxy-thiacalix[4]arene-26,28-diol (*cone*) 4a

Compound **3a** (60 mg, 0.09 mmol) was dissolved in 20 ml of ethanol and refluxed with $SnCl_2 \cdot 2H_2O$ (205 mg, 0.9 mmol) overnight. The end of reaction was checked by TLC (DCM). Then solvent was evaporated under reduced pressure, the solid residue dissolved in DCM and washed with 1 M aqueous KOH and then with water. The organic layer was dried over $MgSO_4$, after filtration the solvent was removed under vacuum. The product was obtained as a grey solid (25 mg, 45%), which was used in the next step without further purification. Mp: 229–232 °C (decomp.). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.01 (s, 4H, H-arom(NH_2)), 6.83 (d, 4H, J=8.5 Hz, *m*-H-arom), 6.69 (s, 2H, –OH), 6.46 (t, 2H, J=7.8 Hz, *p*-H-arom), 4.27 (t, 4H, J=6.8 Hz, –O–CH_2–), 3.54 (br s, 4H, –NH_2), 1.96 (m, 4H, –OCH_2–CH_2–), 1.10 (t, 6H, J=7.3 Hz, –CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 158.1, 150.5, 138.0, 134.3, 129.6, 124.7, 123.2, 123.1, 80.0, 23.2, 10.4. IR (KBr) ν cm^{-1}: 3419, 2963, 2926, 1618, 1563, 1445, 1431, 1384, 1326, 1229. MS-ESI$^+$ *m*/*z*: 633.07 [M+Na]$^+$.

4.5. Synthesis of 5,17-diamino-25,27-dipropoxycalix[4]-arene-26,28-diol (*cone*) 4b

Dinitrocalix[4]arene **3b** (477 mg, 0.80 mmol) was dissolved in 150 ml of ethyl acetate, catalytic amount of Pd/C (10%) was added and the mixture was stirred overnight under hydrogen atmosphere. The course of reaction was checked by TLC (petroleum ether/EtOAc=3:1). After the starting compound (R_f=0.8) has disappeared from the reaction mixture, catalyst was filtered off over short Celite column. Finally, solvent was removed on vacuum evaporator to yield 400 mg (93%) of title compound[16] as beige solid, which was used in the next step without further purification. Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.66 (s, 2H, OH), 6.91 (d, 4H, J=7.5 Hz, *m*-H-arom), 6.74 (t, 2H, J=7.4 Hz, *p*-H-arom), 6.46 (s, 4H, (H_2N)-*H-arom*), 4.29 (d, 4H, J=13.0 Hz, Ar–CH_2–Ar *ax.*), 3.93 (t, 4H, J=6.4 Hz, –O–CH_2–), 3.23 (d, 4H, J=12.9 Hz, Ar–CH_2–Ar *eq.*), 2.97 (br s, 4H, –NH_2), 2.04 (m, 4H, –OCH_2–CH_2–), 1.26 (t, 6H, J=7.4 Hz, –CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 151.9, 146.0, 137.8, 133.5, 128.9, 128.6, 124.9, 115.8, 78.1, 31.3, 23.3, 10.7.

4.6. Synthesis of 5,17-bis[*N*′-(4-methylphenyl)ureido]-25,27-dipropoxythiacalix[4]arene-26,28-diol (*cone*) 6a

Diaminothiacalixarene **4a** (0.164 mmol) was dissolved in 20 ml of dry DCM and stirred under nitrogen with isocyanate **5a** (0.984 mmol) for 4 days at room temperature. To quench the reaction, methanol (30 ml) was added and the mixture was stirred for 15 min. Solvents were then removed under reduced pressure and the resulting solid was triturated with 40 ml of MeOH/DCM=40:1 mixture. The product in the form of white precipitate was collected by filtration, washed with methanol and dried. Yield: 40%, mp: >350 °C (decomp.). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.57 (s, 2H, –NH–), 8.56 (s, 2H, –NH–), 7.78 (s, 4H, H-arom), 7.38 (2H, s, –OH), 7.34 (d, 4H, J=8.1 Hz, H-arom), 7.08 (d, 4H, J=8.1 Hz, H-arom), 7.02 (d, 4H, J=8.0 Hz, H-arom), 6.70 (t, 2H, J=7.6 Hz, *p*-H-arom), 4.30 (t, 4H, J=6.4 Hz, –O–CH_2–), 2.24 (s, 6H, Ar–CH_3), 1.89 (m, 4H, –OCH_2–CH_2–), 1.08 (t, 6H, J=7.4 Hz, –CH_2–CH_3). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 157.95, 152.64, 152.20, 136.99, 135.05, 131.64, 130.59, 129.06, 128.63, 126.49, 125.30, 121.74, 118.33, 76.67, 22.80, 20.23, 10.29. IR (KBr) ν cm^{-1}: 3386, 2964, 2924, 1654, 1594, 1543, 1517, 1451, 1427, 1406, 1385, 1313, 1225. MS-ESI$^+$ *m*/*z*: 899.19 [M+Na]$^+$. Anal. Calcd for $C_{46}H_{44}N_4O_6S_4$: C, 62.99; H, 5.06; N, 6.39; S, 14.62%. Found: C, 62.60; H, 4.91; N, 6.19%.

4.7. Synthesis of 5,17-bis[*N*′-(4-methylphenyl)ureido]-25,27-dipropoxycalix[4]arene-26,28-diol (*cone*) 7a

Prepared by the same procedure as described for **6a** using **4b** and **5a** as starting compounds. Yield: 59%, mp: >350 °C (decomp.). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.38 (br s, 2H, –NH–), 8.25 (br s, 2H, –NH–), 8.15 (br s, 2H, –OH), 7.30 (d, 4H, J=7.6 Hz, H-arom), 7.18 (s, 4H, H-arom), 7.04 (m, 8H, H-arom), 6.81 (t, 2H, J=7.4 Hz, H-arom), 4.19 (d, 4H, J=12.6 Hz, Ar–CH_2–Ar *ax.*), 3.94 (t, 4H, J=5.6 Hz, –O–CH_2–CH_2–), 3.39 (d, 4H, J=12.6 Hz, Ar–CH_2–Ar *eq.*), 2.23 (s, 6H, Ar–CH_3), 2.00 (m, 4H, –CH_2–CH_3), 1.31 (t, 6H, J=7.2 Hz, –CH_2–CH_3). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 152.74, 151.81, 147.85, 137.41, 133.85, 131.10, 130.22, 129.10, 128.81, 127.89, 125.21, 119.42, 118.08, 78.10, 30.61, 23.06, 20.33, 10.83. IR (KBr) ν cm^{-1}: 3405, 2962, 2925, 1656, 1604, 1548, 1516, 1484, 1458, 1385, 1313, 1245, 1201. MS-ESI$^+$ *m*/*z*: 827.31 [M+Na]$^+$. Anal. Calcd for $C_{50}H_{52}N_4O_6$: C, 74.60; H, 6.51; N, 6.96%. Found: C, 74.92; H, 6.24; N, 7.11%.

4.8. Synthesis of 5,17-bis[*N*′-(4-nitrophenyl)ureido]-25,27-dipropoxycalix[4]arene-26,28-diol (*cone*) 7b

Prepared by the same procedure as described for **6a** using **4b** and **5b** as starting compounds. Yield: 28%, mp: 259–261 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 9.30 (br s, 2H, –NH–), 8.48 (br s, 2H, –NH–), 8.36 (br s, 2H, –OH), 8.17 (d, 4H, J=9.0 Hz, H-arom), 7.67 (d, 4H, J=9.0 Hz, H-arom), 7.23 (s, 4H, H-arom), 7.04 (d, 4H, J=7.5 Hz, H-arom), 6.83 (t, 2H, J=5.9 Hz, H-arom), 4.20 (d, 4H, J=11.1 Hz, Ar–*C*H_2–Ar *ax.*), 3.95 (br t, 4H, –O–***C****H*$_2$–CH_2–), 3.42 (d, 4H, J=13.5 Hz, Ar–CH_2–Ar *eq.*), 2.01 (br m, 4H, –***C****H*$_2$–CH_3), 1.31 (br t, 6H, –CH_2–***C****H*$_3$). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 152.00, 151.78, 148.45, 146.70, 140.65, 133.73, 130.19, 128.80, 127.96, 125.10, 119.92, 117.20, 117.18, 78.25, 30.58, 23.03, 10.79. IR (KBr) ν cm^{-1}: 3392, 2964, 2931, 1681, 1612, 1599, 1552, 1506, 1484, 1461, 1329, 1304, 1249, 1211. MS-ESI$^+$ *m*/*z*: 889.28 [M+Na]$^+$. Anal. Calcd for $C_{48}H_{46}N_6O_{10}$: C, 66.50; H, 5.35; N, 9.69%. Found: C, 66.18; H, 5.61; N, 9.52%.

4.9. Crystallographic data for 3a′

$C_{30}H_{26}N_2O_8S_4$, M=670.81 g mol^{-1}, triclinic system, space group *P*-1, a=8.390(2) Å, b=9.280(3) Å, c=10.512(3) Å, α=113.86(3)°, β=89.09(2)°, γ=101.38(3)°, Z=1, V=731.8(4) Å^3, D_c=1.522 g cm^{-3}, μ(Cu Kα)=3.467 mm^{-1}, crystal dimensions of 0.13×0.27×0.51 mm. Data were collected at 150(2) K on a Xcalibur PX diffractometer

with graphite monochromated Cu Kα radiation. The structure was solved by direct methods[17] using the CRYSTALS suite of programs[18] and anisotropically refined by full-matrix least-squares on F values to final R=0.0604 and R_w=0.0724 using 11,645 independent reflections (θ_{max}=76.483°) and 199 parameters. At the end of refinement, hydrogen atoms were placed in calculated positions. Crystallographic data were deposited in CSD under CCDC registration number 675371.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.030.

References and notes

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