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Anion receptors based on ureidocalix[4]arenes immobilised in the *partial cone* conformation†

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A novel method enabling the synthesis of receptors based on the calix[4]arenes immobilized in the *partial cone* conformation is reported. The application of a protection/deprotection strategy using nosyl groups enables the regioselective introduction of functional groups (NO_2 and NH_2) into the upper rim of calix[4]arenes, leading finally to the substitution pattern so far inaccessible to calixarene chemistry. The introduction of two ureido functions at the *para* positions of the *partial cone* conformer yields a novel type of receptor which can bind anions even in a highly competitive solvent (DMSO). This revealed that the *partial cone* conformation, so far rather ignored in supramolecular chemistry, can be also very useful in design of novel anion receptors.

Introduction

The importance of anions in various biological systems is well recognised. Hence, the study of the complexation of anionic species plays an important role in contemporary supramolecular chemistry as witnessed by many review articles[1] and books[2] published recently. Given the importance of anions in chemistry, medicine, environmental pollution or industrial processes, much effort has been focused on the design of anion binding ligands, receptors and sensors.[3]

Not surprisingly, the main strategy for anion recognition relies on the application of positively charged species like polyammonium, guanidinium, or quaternary ammonium salts,[4] which can bind anions mainly *via* electrostatic interactions. On the other hand, neutral organic receptors for anion recognition *via* hydrogen bonding interactions are especially useful in the design. These receptors can use highly directional hydrogen bonds from amide, sulfonamide, urea or thiourea moieties[5] which can effectively interact with anions, especially if they are suitably preorganised. From this point of view, calix[4]arenes[6] offer many possibilities due to their tuneable 3D shapes of the molecule leading to four different conformations (*cone*, *partial cone*, *1,3-alternate*, and *1,2-alternate*) (Fig. 1). This makes calix[4]arenes ideal candidates for the role of molecular scaffolds in the design of novel receptors allowing the elaborated introduction of various functional groups into precisely defined mutual positions.

Many neutral calixarene-based ligands for anion recognition have been reported in the literature so far.[7,8] We have previously focused on a series of arylamide- or arylureido-substituted calix[4]arenes[9] which can be used for anion recognition in solution. The systematic study of ureidocalix[4]arenes revealed that bis(phenylureido)-calix[4]arene immobilised in the *cone* conformation[10] can bind benzoate with surprisingly high selectivity. On the other hand, receptors in the 1,3-alternate conformation bearing four ureido functions bind anions with a negative allosteric effect[11] where only one site of the molecule is capable of forming a complex. Interestingly, albeit there are many references for the *cone* or *1,3-alternate* conformations, there is almost no precedence[9d,12] of using anion receptors in the remaining two conformations – *partial cone* or *1,2-alternate*.

While the *1,2-alternate* is scarcely used because of the lack of general synthetic methods leading to this conformation, preparation of the *partial cone* isomers is relatively easy. The problem lies in the wrong mutual positions of nitro groups used as the starting point for subsequent derivatization. Usually we start with distally disubstituted calix[4]arenes (Scheme 1, path a), where subsequent nitration and

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† Electronic supplementary information (ESI) available: ^{1}H NMR, ^{13}C NMR, COSY, HMBC, HMQC and NOE spectra of compound **4**, including complete structure assignment of this compound. CCDC 894549. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2nj40724h

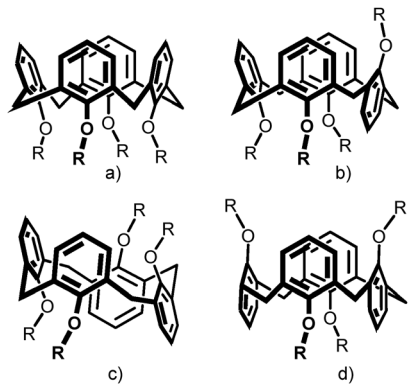
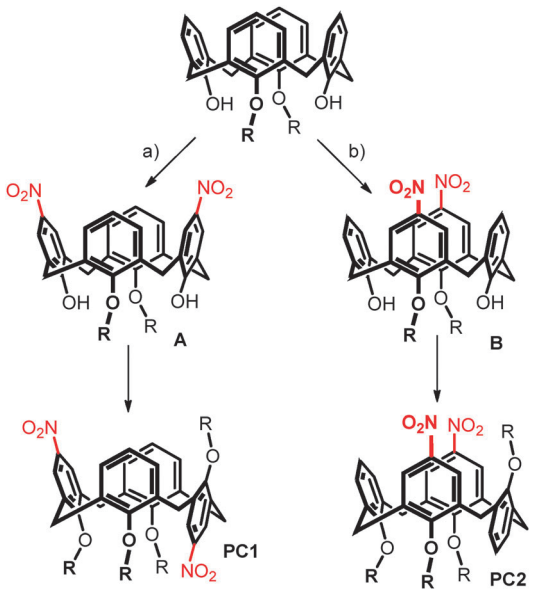


Fig. 1 Four basic conformations of calix[4]arene: (a) *cone*, (b) *partial cone*, (c) *1,2-alternate* and (d) *1,3-alternate*.



Scheme 1 Two different substitution patterns in dinitro substituted *partial cone* calix[4]arenes: (a) common nitration followed by alkylation and (b) nitration using nosyl protection/deprotection method followed by alkylation.

final alkylation of dinitro intermediate **A** leads to substitution pattern **PC1**. Unfortunately, this *partial cone* conformer bears nitro groups on the opposite sites of the cavity which is not suitable for the design of receptors. Recently we have reported a straightforward regioselective synthesis[13] enabling the preparation of dinitro isomers **B** with the nitro groups on the unsubstituted aromatic rings (Scheme 1, path b). Here we report on the synthesis of novel type of anion receptors based on the calix[4]arenes immobilized in the *partial cone* conformation possessing a **PC2** substitution pattern. These isomers have been so far inaccessible to calixarene chemistry and represent structures which are complementary to commonly used calixarene-based receptors (compare **PC1** and **PC2** in Scheme 1).

Results and discussion

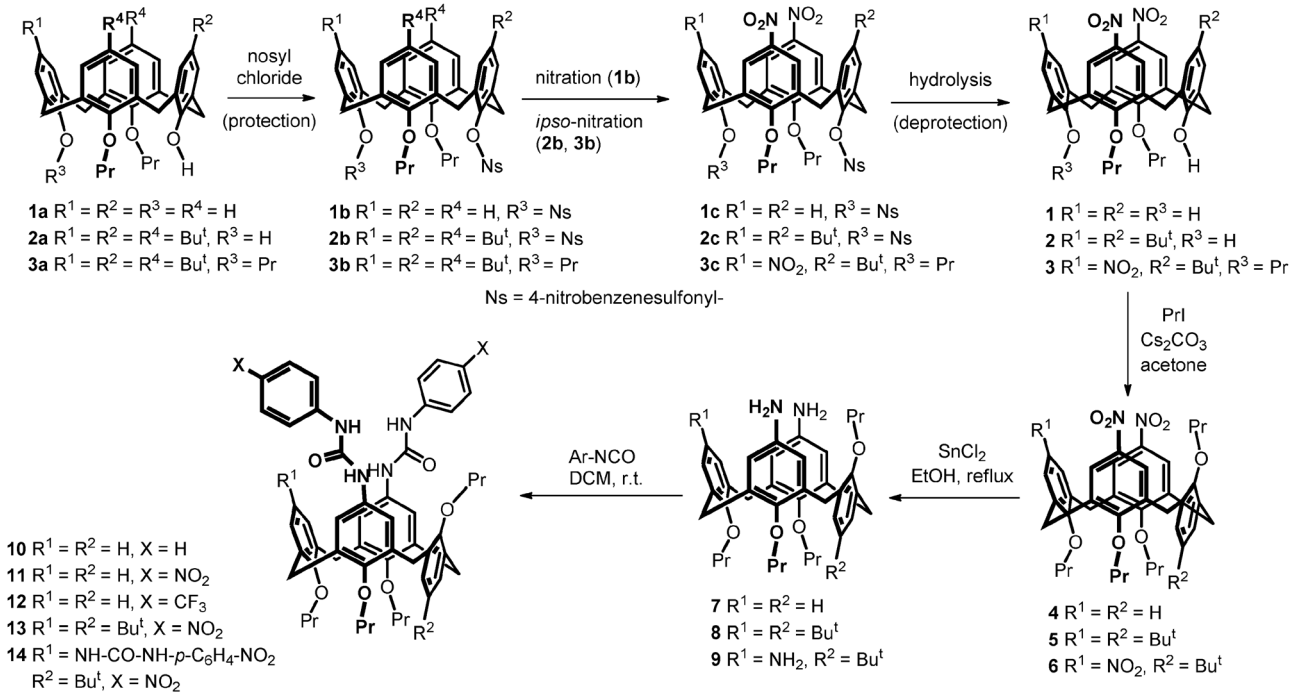
The regioselective introduction of nitro groups into the calixarene skeleton was recently described by our group.[13] The synthetic strategy is based on a direct nitration or *ipso*-nitration of the corresponding nosyl-substituted derivatives **1b–3b**. As the reactivity of alkoxy substituted aromatic rings is higher compared to that of aromatic units bearing nosyl groups, one can selectively introduce nitro groups at the *para* positions of alkylated aromatic subunits. The whole strategy consists of three basic steps: (i) lower-rim protection (introduction of a nosyl moiety) leading to the formation of compounds **1b–3b**, (ii) nitration or *ipso*-nitration (depending on the upper rim substitution) to form **1c–3c**, and (iii) deprotection of the nosyl group by an alkaline hydrolysis to yield **1–3**. This procedure straightforwardly (overall yield for the transformation of **1a** to **1** is 75%) leads to the substitution pattern (Scheme 1) which is so far inaccessible to calix[4]arene chemistry and which is complementary to the commonly used isomers (Scheme 2).

The isomers **1–3** were then used for the formation of the *partial cone* conformers. The alkylation with propyl iodide using Cs_2CO_3 as a base led always to the mixture of the *partial cone* and *cone* isomers in approximately 95 : 5 ratio. Unfortunately, these mixtures could not be separated by column chromatography either on silica gel or on alumina. On the other hand, a simple precipitation from CH_2Cl_2–MeOH system gave pure *partial cone* isomers **4–6** in medium yields (≈40%).

The conformation of **4–6** was confirmed using ^{1}H NMR spectroscopy. The *partial cone* conformer can be imaginary bisected into two halves – one having the *cone*-like arrangement with the *syn* orientation of the aromatic units, and the second one possessing the *1,3-alternate*-like features (*anti* oriented phenolic rings). Both halves retained their typical splitting pattern and signal multiplicity known from ^{1}H NMR spectra of common conformers. Thus, dinitro derivative **4** (Fig. 2) showed one doublet at 3.12 ppm for equatorial CH bond of the bridging CH_2 moiety, and another doublet at 4.06 ppm for the axial CH bond, both with typical geminal interaction constants (J = 13.8 Hz). On the other hand, signals of bridging units in the *1,3-alternate*-like part of the molecule possess almost identical chemical shifts (≈3.72 ppm). While the propyl group in the *1,3-alternate*-like half of the molecule exhibits typical shifts (Fig. 2), the analogous signals of the opposite propyl group in the *cone*-like part are distinctly shifted towards the stronger field (upfield shift). This indicates that protons H^a–H^c are located close to the distal inverted aromatic unit which leads to substantial shielding of all aliphatic signals due to the magnetic anisotropy of the aromatic system (for total structure assignment see ESI†).

Thus, the comparison of the corresponding chemical shifts (Fig. 2) clearly shows the substantial upfield shift (approx. 0.60 ppm) for all protons (compare 3.84 ($H^{a'}$)/3.25 (H^a) ppm for –OCH_2– moiety, or 1.15 ($H^{c'}$)/0.69 (H^c) ppm for terminal CH_3 group). Similar features and trends can be observed in all newly prepared derivatives **4–14** possessing the *partial cone* conformation (for complete structure assignment of compound **4**, see ESI†).

The final unambiguous structural evidence for compound **5** was obtained by X-ray crystallographic analysis of monocrystals grown from the methanol–CH_2Cl_2 mixture. The molecule adopts a *partial cone* conformation (Fig. 3) where the aromatic



Scheme 2 Synthesis of calixarene-based receptors in the *partial cone* conformation.

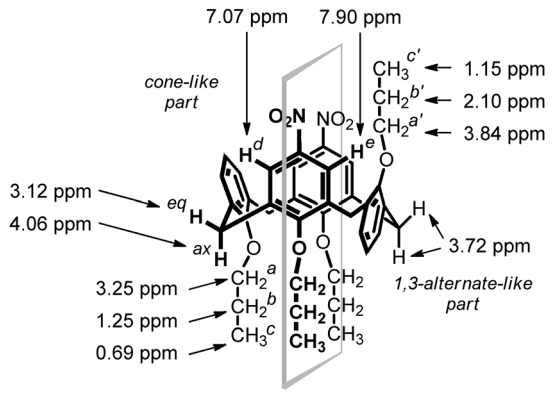


Fig. 2 Typical features of the ^{1}H NMR spectra of derivative **4** ($CDCl_3$, 298 K, 300 MHz).

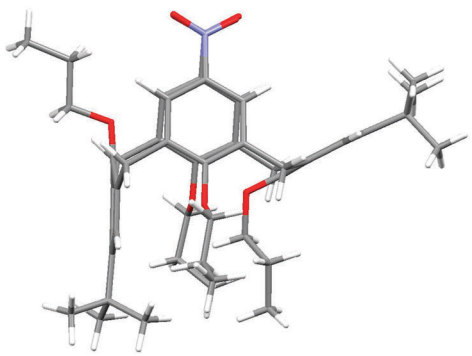


Fig. 3 X-Ray structure of derivative **5**.

units bearing NO_2 groups are pointing towards each other into the cavity, and the third aromatic unit with the *syn* orientation is almost ideally perpendicular (89.06(8)°) to the main plane formed by the four carbon bridging atoms. The remaining *anti*-oriented aromatic unit is noticeably tilted from the cavity with the interplanar angle = 151.10(8)° (with the main plane). Interestingly, both nitro groups are slightly turned out from the ideal coplanar arrangement with attached aromatic units by 10.1(3)° and 15.9(3)°.

Nitro derivatives **4–6** were then smoothly reduced with $SnCl_2{\cdot}2H_2O$ in refluxing ethanol to give amino derivatives **7**, **8** and **9** in 95, 97, and 98% yields, respectively. Target receptors **10–14** were obtained by the reaction of amines **7–9** with appropriate isocyanates (phenyl, *p*-trifluoromethylphenyl or *p*-nitrophenyl) in dichloromethane at room temperature and they were isolated in 63–78% yields (for **10–13**) and 31% yield (for **14**).

The complexation ability of ligands **10–13** was studied by standard ^{1}H NMR titration experiments using an increasing concentration of appropriate anions to obtain different calixarene : anion ratios (1 : 0.3–10). To avoid possible unwanted interactions of receptors with counter-cations all anions studied were used in the form of tetrabutylammonium salts. In the beginning, the ^{1}H NMR titration experiments were performed in the mixed solvent ($CDCl_3$/CD_3CN = 4 : 1, v/v) to ensure the solubility of both organic and inorganic parts. Under these conditions, the addition of anions to the receptor led to the remarkable down-field shifts of ureido NH signals thus indicating the complexation phenomenon under fast exchange conditions. Very high complexation induced chemical shifts (CIS) were observed for chloride and bromide (>3 ppm). Unfortunately, the binding constants were too high ($K \gg 10^4$) to be reliably measured by the NMR technique.[14]

Based on these preliminary results, we decided to change the solvent system for more polar DMSO-d_6. Despite the usage of this highly competitive solvent towards hydrogen bonding

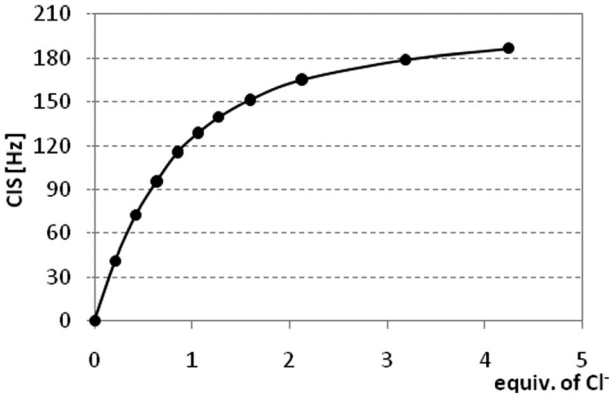


Fig. 4 binding isotherm of receptor **12** with a chloride anion (^{1}H NMR titration, 300 MHz, 298 K, DMSO-d_6).

interactions, reasonable CIS values for NH protons were observed for all anions measured. Thus, CIS value for the **11**/AcO^- system was 1.50 ppm and similar values were obtained for all receptors with benzoate and acetate, while other anions usually showed lower values (compare CIS = 0.65 for the **11**/Cl^- system). The binding constants were determined from the CIS values of NH protons, Fig. 4 shows a typical binding isotherm constructed for **12**/Cl^- system. All titration curves (with exception of receptor **14** bearing three ureido moieties) best fit with the formation of 1 : 1 complexes (calix/anion), the stoichiometry was also proved by the independent Job plot analysis[15] for selected anions (Fig. 5). The calculated binding constants are summarised in Table 1.

All ureido or amidic receptors for anions are known to operate *via* the hydrogen bonds between the N–H moiety and negatively charged species (N–H$\cdots$A$^-$). Albeit DMSO is known as a highly competitive solvent towards HB interactions, the binding constants of receptors **10–13** are surprisingly high. In all cases, the carboxylates possess the highest binding constants, with selectivity for benzoate over acetate (for **11–13**). Thus, both receptors **11** and **12** bearing electron withdrawing substituents (NO_2 and CF_3) possess almost the same complexation ability towards benzoate ($K_{Bz} \approx 16\,000$ M^{-1}), while the complexation of acetate is reasonably different $K_{Ac} = 13\,000$ M^{-1} for **12** and $K_{Ac} = 2250$ M^{-1} for **11**. This leads to selectivity factor (K_{Bz}/K_{Ac}) 1.23 for **12** and 7.33 for **11**. The only exception is represented by the unsubstituted receptor **10** showing higher selectivity for acetate ($K_{Bz} = 2750$ M^{-1}, $K_{Ac} = 6400$ M^{-1}).

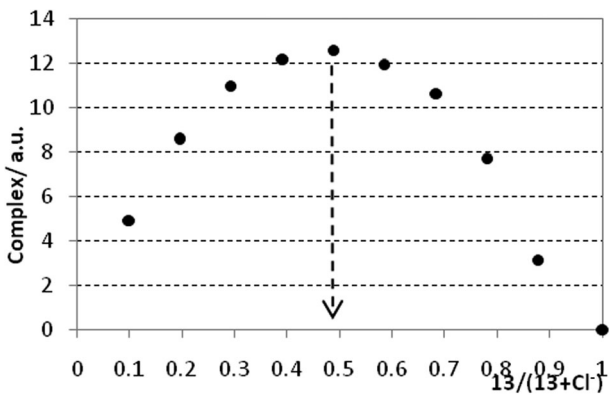


Fig. 5 Job plot for system **13**/Cl^- in DMSO-d_6 (^{1}H NMR titration, 300 MHz, 298 K).

Table 1 Binding constants of receptors **10–13** towards selected anions (^{1}H NMR titration, 300 MHz, DMSO-d_6, 298 K)

	K/M^{-1}			
Anion	**10**	**11**	**12**	**13**
Cl^-	870 ± 200	1540 ± 370[c]	450 ± 50	800 ± 180
Br^-	120 ± 40	920 ± 100	60 ± 10	210 ± 80
I^-	[a]	30 ± 6	[a]	175 ± 40
AcO^-	6400 ± 560	2250 ± 300	13 000 ± 3000	2700 ± 650
BzO^-	2750 ± 390	16 500 ± 3500	16 000 ± 2800	6200 ± 1200
CN^-	50 ± 13	730 ± 120	240 ± 50	680 ± 150
NO_3^-	120 ± 20	380 ± 70	28 ± 7	[a]
DMSO-d_6[b]	8 ± 2	12 ± 3	11 ± 1	7 ± 2

[a] Too small changes in chemical shifts upon addition of anions. [b] Titration experiments were carried out in pure $CDCl_3$. [c] The complexation constant for the *cone* analogue of receptor **11** (measured for the comparison): $K_{Cl} = 173 \pm 24$ M^{-1}.

As follows from Table 1, the binding site created by two preorganised ureido functions can bind also other anions possessing various geometries. Thus, a linear cyanide anion is efficiently bound by **11** ($K_{CN} = 730$ M^{-1}) or by **13** ($K_{CN} = 680$ M^{-1}). The binding constants for spherical halides are inversely related to their basicity as can be documented by the results for compound **11**: $K_{Cl} = 1540$ M^{-1}, $K_{Br} = 920$ M^{-1}, and $K_I = 30$ M^{-1}.

Receptor **14** bearing three ureido functions on the upper rim was inefficient towards NO_3^- and CN^- anions. On the other hand, halogens or carboxylates showed rather complicated behaviour which did not correspond to the formation of complexes possessing 1 : 1 stoichiometry. We have also studied the interaction of receptors with solvent used – DMSO. The ^{1}H NMR titrations of receptors **10–13** with DMSO-d_6 was carried out in $CDCl_3$ and the corresponding complexation constants are shown in Table 1. As the K values are very small (<12 M^{-1}), these interactions were neglected in experiments carried out using DMSO-d_6 as solvent.

Conclusions

A novel method enabling the synthesis of receptors based on the calix[4]arenes immobilized in the *partial cone* conformation is reported. The application of a protection/deprotection strategy using nosyl groups enables the regioselective introduction of functional groups (NO_2 and NH_2) into the upper rim of calix[4]arenes, leading finally to the substitution pattern so far inaccessible to calixarene chemistry, and structurally complementary to commonly used calixarene-based receptors The introduction of two ureido functions at the *para* positions of calix[4]arenes immobilised in the *partial cone* conformation gave a novel type of receptor used successfully for the complexation of anions.[18] Albeit based on the hydrogen-bonding interactions, these receptors can bind anions even in a highly competitive solvent like DMSO. The complexation study revealed that the *partial cone* conformation, so far rather

ignored in supramolecular chemistry, can be very useful in design of novel anion receptors.

Experimental

Materials and instrumentations

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled using conventional methods. Melting points were measured on a Heiztisch Mikroskop-Polytherm A (Wagner & Munz, Germany). NMR spectra were performed on Varian Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and on Bruker Avance DRX 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers. Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm and are referred to the TMS as an internal standard; coupling constants (J) are in Hz. The signal assignment was supported by ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC or ^{1}H–^{13}C HMBC 2D NMR and 1D ^{1}H–DPFGSE NOE experiments using the standard pulse sequences provided by Bruker. The mass analyses were performed using ESI technique on a Q-TOF (Micromass) spectrometer. Elemental analyses were done on Perkin-Elmer 240, Elementar vario EL (Elementar, Germany) or Mitsubishi TOX-100 instruments. All samples were dried in the desiccator over P_2O_5 under vacuum (1 Torr) at 80 °C for 8 hours. The IR spectra were measured on an FT-IR spectrometer Nicolet 740 or Bruker IFS66 spectrometers equipped with a heatable Golden Gate Diamante ATR-Unit (SPECAC) in KBr. 100 Scans for one spectrum were co-added at a spectral resolution of 4 cm^{-1}. The courses of the reactions were monitored by TLC using TLC aluminum sheets with Silica gel 60 F254 (Merck). The column chromatography was performed using Silica gel 60 (Merck).

Synthesis

All intermediates **1a–1c**, **2a–2c**, **3a–3c** and **1–3** were prepared according to the recently published procedures.[13]

General procedure: synthesis of 25,26,27,28-tetrapropoxy derivatives 4–7 in the *partial cone* conformation

The corresponding calix[4]arene derivatives **1–3** were dissolved in anhydrous acetone (200 ml for 1 g), then powdered Cs_2CO_3 (2 equiv. for each hydroxyl group) and 1-iodopropane (3 equiv. for each hydroxyl group) were added. The mixture was heated to reflux for 3 days (monitored by TLC), and the solvent was removed under reduced pressure. The residue was acidified with 1 M hydrochloric acid and extracted twice with CH_2Cl_2. The combined organic layers were washed with water, then with brine and dried over $MgSO_4$. Organic solvent was evaporated to dryness. The further purification is described below for each particular derivative.

5,17-Dinitro-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*, *syn*-dinitro) 4

A general procedure was applied to 5,17-dinitro-26,28-dipropoxycalix[4]arene-25,27-diol **1** (0.50 g, 0.84 mmol), Cs_2CO_3 (1.09 g, 3.35 mmol) and 1-iodopropane (0.5 ml, 5.13 mmol). The residue after evaporation was dissolved in 2 ml of CH_2Cl_2 and precipitated by addition of 50 ml of methanol. The precipitate was filtered off, dissolved in 2 ml of CH_2Cl_2, and then the whole procedure was repeated two more times, the third precipitate was air dried to give 0.23 g of product **4** as a white powder in 40% yield, mp: 197–198 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 7.87 (2H, d, J = 2.9 Hz, Ar*H*), 7.23 (2H, d, J = 7.6 Hz, Ar*H*), 7.17 (2H, d, J=7.6 Hz, Ar*H*), 7.09 (2H, d, J = 2.9 Hz, Ar*H*), 7.02 (1H, t, J = 7.5 Hz, Ar*H*), 6.92 (1H, t, J = 7.5 Hz, Ar*H*), 4.06 (2H, d, J = 13.8 Hz, ArCH_2Ar *ax*), 3.86–3.59 (10H, m, 3 × OCH_2 + 2 × ArCH_2Ar), 3.29–3.21 (2H, m, OCH_2), 3.12 (2H, d, J = 14.1 Hz, ArCH_2Ar *eq*), 2.14–2.06 (2H, m, OCH$_2$CH_2), 1.95–1.83 (4H, m, OCH$_2$CH_2), 1.29–1.21 (2H, m, OCH$_2$CH_2), 1.17–1.08 (9H, m, CH_3), 0.69 (3H, t, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 161.1, 157.4, 156.5, 142.3, 136.1, 135.5, 133.3, 133.2, 131.0, 130.0, 125.1, 123.8, 122.6, 76.9, 75.8, 75.5, 35.7, 30.9, 24.1, 24.0, 22.5, 11.0, 10.9, 9.4; TOF HRMS (ESI+): calcd for $[C_{40}H_{46}N_2O_8 + Na]^+$: 705.3146. Found: m/z (rel. int%) 705.3146 (100) $[M + Na]^+$. For complete structure assignment using various NMR techniques, see ESI.†

5,17-Di-*tert*-butyl-11,23-dinitro-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*, *syn*-dinitro) 5

A general procedure was applied to 11,23-di-*tert*-butyl-5,17-dinitro-26,28-dipropoxycalix[4]arene-25,27-diol **2** (1.00 g, 1.41 mmol), Cs_2CO_3 (1.83 g, 5.62 mmol) and 1-iodopropane (0.82 ml, 8.41 mmol). The residue after evaporation was dissolved in 2 ml of CH_2Cl_2, then 40 ml of methanol was added and the resulting solution was stored at 0 °C overnight. The crystals formed were filtered off, quickly washed with cold methanol and air dried to give 0.50 g of product **5** as a yellowish powder in 45% yield, mp: 237–240 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 7.86 (2H, d, J = 2.9 Hz, Ar*H*), 7.21 (2H, s, Ar*H*), 7.15–7.13 (4H, m, Ar*H*), 4.09 (2H, d, J = 13.5 Hz, ArCH_2Ar *ax*), 3.80–3.57 (10H, m, 3 × OCH_2 + 2 × ArCH_2Ar), 3.33–3.27 (2H, m, OCH_2), 3.10 (2H, d, J = 13.8 Hz, ArCH_2Ar *eq*), 2.06–1.98 (2H, m, OCH$_2$CH_2), 1.96–1.84 (4H, m, OCH$_2$CH_2), 1.41–1.32 (20H, m, OCH$_2$CH_2 + 2 × *But*), 1.12–1.05 (9H, m, CH_3), 0.65 (3H, t, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 296 K) δ: 161.3, 155.2, 153.4, 146.5, 144.5, 142.2, 135.4, 135.4, 133.5, 132.2, 127.7, 126.6, 125.3, 123.9, 76.9, 74.9, 74.8, 36.5, 34.5, 34.3, 31.8, 31.5, 24.1, 23.8, 21.6, 11.0, 10.8, 9.9; TOF HRMS (ESI+): calcd for $[C_{48}H_{62}N_2O_8 + Na]^+$: 817.4398. Found: m/z (rel. int. %) 817.4397 (100) $[M + Na]^+$.

5-*tert*-Butyl-11,17,23-trinitro-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 6

A general procedure was applied to 5-*tert*-butyl-11,17,23-trinitro-26,27,28-tripropoxycalix[4]arene-25-ol **3** (0.80 g, 1.08 mmol), Cs_2CO_3 (0.70 g, 2.15 mmol) and 1-iodopropane (0.30 ml, 3.08 mmol). The residue after evaporation was dissolved in 2 ml of CH_2Cl_2, then 40 ml of methanol was added and the resulting solution was stored at 0 °C overnight. The crystals formed were filtered off, quickly washed with cold methanol and air dried to give 0.30 g of product **6** as a white powder in 35% yield, mp: 222–224 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 8.11 (2H, s, Ar*H*), 7.92 (2H, d, J = 2.6 Hz, Ar*H*), 7.24 (2H, s, Ar*H*), 7.12 (2H, d, J = 2.6 Hz, Ar*H*), 4.16 (2H, d, J = 13.8 Hz, ArCH_2Ar *ax*), 3.85–3.58 (10H, m, 3 × OCH_2 + 2 × ArCH_2Ar), 3.44–3.39

(2H, m, OCH_2), 3.28 (2H, d, J = 14.1 Hz, ArCH_2Ar *eq*), 2.09–1.86 (6H, m, OCH$_2$CH_2), 1.37–1.30 (11H, m, OCH$_2$CH_2 + *Bu*^{t}), 1.13–1.06 (9H, m, CH_3), 0.67 (3H, t, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 296 K) δ: 161.7, 161.3, 155.05, 144.7, 143.0, 142.4, 137.4, 134.0, 133.6, 132.0, 127.8, 126.0, 125.2, 123.4, 77.2, 75.2, 75.0, 36.4, 34.3, 31.8, 31.2, 24.0, 23.9, 21.8, 11.0, 10.7, 10.0; TOF HRMS (ESI+): calcd for $[C_{44}H_{53}N_3O_{10} + Na]^+$: 806.3623. Found: m/z (rel. int. %) 806.3627 (100) $[M + Na]^+$.

General procedure: reduction of nitro derivatives 4–6

The corresponding nitro derivatives **4–6** were dispersed in ethanol (10 ml for 100 mg) and $SnCl_2{\cdot}2H_2O$ (5 equiv. for each nitro group) was added. The mixture was heated to reflux overnight and then poured into 1 M NH_3 (aq.). Resulting suspension was repeatedly extracted with CH_2Cl_2, combined organic layers were washed with water, then with brine and dried over $MgSO_4$. Organic solvent was removed under reduced pressure to give the pure products **7–9**.

5,17-Diamino-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*, *syn*-diamino) 7

A general procedure was applied to dinitro derivative **4** (0.43 g, 0.63 mmol), $SnCl_2{\cdot}2H_2O$ (1.42 g, 6.30 mmol). The product **7** was isolated as a brown powder (0.37 g) in 95% yield, mp: 176–179 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 7.20 (2H, d, J = 7.6 Hz, ArH), 7.05 (2H, d J = 7.3 Hz, ArH), 6.87 (1H, t, J = 7.0 Hz, ArH), 6.83 (1H, t, J = 7.5 Hz, ArH), 6.45 (2H, d, J = 2.6 Hz, ArH), 5.61 (2H, d, J = 2.6 Hz, ArH), 4.04 (2H, d, J = 13.5 Hz, ArCH_2Ar *ax*), 3.75–3.45 (10H, m, 3 × OCH_2 + 2 × ArCH_2Ar), 3.29–3.23 (2H, m, OCH_2), 2.96 (2H, d, J = 13.5 Hz, ArCH_2Ar *eq*), 2.00–1.93 (2H, m, OCH$_2$CH_2), 1.89–1.77 (4H, m, OCH$_2$CH_2), 1.42–1.34 (2H, m, OCH$_2$CH_2), 1.14–1.07 (9H, m, 3 × CH_3), 0.68 (3H, t, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 296 K) δ: 157.7, 149.5, 140.3, 137.4, 134.3, 134.1, 132.9, 130.5, 129.1, 122.0, 121.9, 118.1, 116.1, 76.4, 75.6, 74.8, 35.9, 31.0, 24.6, 24.0, 22.6, 11.2, 11.1, 9.6; TOF HRMS (ESI+): calcd for $[C_{40}H_{50}N_2O_4 + H]^+$: 623.3843. Found: m/z (rel. int. %) 623.3847 (100) $[M + H]^+$.

5,17-Diamino-11,23-di-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*, *syn*-diamino) 8

A general procedure was applied to dinitro derivative **5** (0.30 g, 0.38 mmol), $SnCl_2{\cdot}2H_2O$ (0.85 g, 3.77 mmol). The product **8** was isolated as a brown powder (0.27 g) in 97% yield, mp: 104–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 7.17 (2H, s, ArH), 7.01 (2H, s, ArH), 6.42 (2H, d, J = 2.6 Hz, ArH), 5.70 (2H, d, J = 2.9 Hz, ArH), 4.07 (2H, d, J = 13.2 Hz, ArCH_2Ar *ax*), 3.75–3.63 (2H, m, OCH_2), 3.58 (4H, d, J = 4.7 Hz, ArCH_2Ar), 3.52–3.44 (2H, m, OCH_2), 3.36–3.30 (4H, m, OCH_2), 2.94 (2H, d, J = 13.5 Hz, ArCH_2Ar *eq*), 1.89–1.75 (6H, m, OCH$_2$CH_2), 1.41–1.32 (20H, m, OCH$_2$CH_2 + 2 × *Bu*^{t}), 1.12–1.02 (6H, m, CH_3), 0.91 (3H, t, J = 7.5 Hz, CH_3), 0.63 (3H, t, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 296 K) δ: 155.4, 154.2, 149.9, 144.7, 143.5, 140.0, 136.4, 134.3, 133.3, 133.1, 127.4, 125.8, 118.3, 116.2, 76.5, 74.7, 73.9, 37.0, 36.5, 34.3, 34.2, 31.9, 24.2, 24.0, 21.6, 11.2, 10.6, 9.9; TOF HRMS (ESI+): calcd for $[C_{48}H_{66}N_2O_4 + H]^+$: 735.5095. Found: m/z (rel. int. %) 735.5095 (100) $[M + H]^+$.

5,11,17-Triamino-23-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 9

A general procedure was applied to trinitro derivative **6** (0.25 g, 0.32 mmol), $SnCl_2{\cdot}2H_2O$ (1.08 g, 4.79 mmol). The product **9** was isolated as a dark brown powder (0.22 g) in 98% yield, mp: 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 296 K) δ: 7.16 (2H, s, ArH), 6.44 (2H, s, ArH), 6.41 (2H, d, J = 2.9 Hz, ArH), 5.79 (2H, d, J = 2.6 Hz, ArH), 3.99 (2H, d, J = 12.9 Hz, ArCH_2Ar *ax*), 3.72–3.42 (10H, m, 3 × OCH_2 + 2 × ArCH_2Ar), 3.30–3.25 (2H, m, OCH_2), 2.83 (2H, d, J = 12.9 Hz, ArCH_2Ar *eq*), 1.89–1.77 (6H, m, OCH$_2$CH_2), 1.37–1.32 (11H, m, OCH$_2$CH_2 + *Bu*^{t}), 1.08–0.98 (9H, m, CH_3), 0.63 (3H, t, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K) δ: 155.5, 149.7, 149.6, 143.4, 140.5, 140.0, 137.9, 133.9, 133.1, 133.0, 127.3, 118.3, 116.2, 116.0, 76.5, 74.9, 73.9, 36.9, 31.9, 31.2, 29.9, 24.3, 24.0, 21.5, 11.1, 10.8, 10.0; TOF HRMS (ESI+): calcd for $[C_{44}H_{59}N_3O_4 + H]^+$: 694.4578. Found: m/z (rel. int. %) 694.4582 (100) $[M + H]^+$.

General procedure: synthesis of calixarene-based receptors 10–14

The amino derivatives **7–9** were dissolved in anhydrous CH_2Cl_2 (30 ml for 0.100 g) under the atmosphere of dry nitrogen. The corresponding isocyanate (2.50 equiv. for each amino group) was added and the mixture was stirred overnight at room temperature. The reaction was quenched by the addition of methanol, then organic solvents were removed under reduced pressure and the residue was purified. The purification method is described below for each particular ligand.

5,17-Bis[*N*′-(phenyl)ureido]-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 10

A general procedure was applied to amino derivative **7** (0.15 g, 0.24 mmol) and phenyl isocyanate (143 mg, 0.13 ml, 1.20 mmol). The product **10** was isolated by column chromatography (30 g of Al_2O_3, eluent CH_2Cl_2/MeOH = 50 : 1, then CH_2Cl_2/MeOH = 1 : 1, R_F = 0.11) as a white powder (0.14 g) in 66% yield, mp: 163–166 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ: 8.36 (2H, s, NH), 8.05 (2H, s, NH), 7.32 (4H, d, J = 7.9 Hz, ArH), 7.22–7.12 (8H, m, ArH), 7.06 (2H, d, J = 2.1 Hz, ArH), 6.91–6.82 (4H, m, ArH), 6.47 (2H, d, J = 2.3 Hz, ArH), 4.00 (2H, d, J = 12.6 Hz, ArCH_2Ar *ax*), 3.76–3.57 (8H, m, OCH_2 + ArCH_2Ar), 3.44–3.30 (4H, m, OCH_2), 3.08 (2H, d, J = 13.5 Hz, ArCH_2Ar *eq*), 1.80–1.64 (6H, m, OCH$_2$CH_2), 1.43–1.23 (2H, m, OCH$_2$CH_2), 1.03 (6H, t, J = 7.3 Hz, CH_3), 0.74 (3H, t, J = 7.2 Hz, CH_3), 0.66 (3H, t, J = 7.6 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 296 K) δ: 157.4, 154.2, 153.4, 139.0, 137.0, 135.3, 133.8, 133.5, 131.0, 130.5, 129.5, 129.1, 124.0, 123.2, 122.7, 122.6, 122.2, 119.6, 76.4, 75.6, 35.5, 31.0, 24.4, 24.0, 22.6, 11.2, 10.9, 9.5; TOF HRMS (ESI+): calcd for $[C_{54}H_{60}N_4O_6 + Na]^+$: 883.4405. Found: m/z (rel. int. %) 883.4402 (100) $[M + Na]^+$.

5,17-Bis[*N*′-(4-nitrophenyl)ureido]-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 11

A general procedure was applied to amino derivative **7** (0.10 g, 0.16 mmol) and 4-nitrophenyl isocyanate (97% purity, 136 mg,

0.80 mmol). The product **11** was isolated by column chromatography (30 g of Al_2O_3, eluent CH_2Cl_2/MeOH = 160 : 1, R_F = 0.14) as a red powder (0.12 g) in 78% yield, mp: 227–230 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ: 8.97 (2H, s, N*H*), 8.10 (2H, s, N*H*), 8.01 (4H, d, J = 9.4 Hz, Ar*H*), 7.43 (4H, d, J = 9.4 Hz, Ar*H*), 7.19–7.13 (6H, m, Ar*H*), 6.91 (1H, t, J = 7.5 Hz, Ar*H*), 6.84 (1H, t, J = 7.5 Hz, Ar*H*), 6.37 (2H, d, J = 2.6 Hz, Ar*H*), 3.99 (2H, d, J = 12.9 Hz, ArCH_2Ar *ax*), 3.77–3.58 (6H, m, OCH_2 + ArCH_2Ar), 3.51–3.39 (4H, m, OCH_2), 3.26 (2H, t, J = 8.2 Hz, OCH_2), 3.08 (2H, d, J = 13.2 Hz, ArCH_2Ar *eq*), 1.85–1.72 (6H, m, OCH$_2$CH_2), 1.40–1.32 (2H, m, OCH$_2$CH_2), 1.05 (6H, t, J = 7.3 Hz, CH_3), 0.87 (3H, t, J = 7.3 Hz, CH_3), 0.66 (3H, t, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 298 K) δ: 157.4, 156.6, 151.6, 151.3, 146.7, 140.6, 136.5, 133.6, 133.2, 132.4, 130.6, 129.1, 125.1, 122.7, 121.3, 120.4, 118.4, 117.1, 75.9, 75.1, 73.8, 36.2, 30.1, 23.4, 23.4, 21.4, 11.0, 10.4, 9.4; TOF HRMS (ESI+): calcd for $[C_{54}H_{58}N_6O_{10} + Na]^+$: 973.4107. Found: m/z (rel. int. %) 973.4101 (100) $[M + Na]^+$. EA found (%) C, 68.14; H, 6.12; N, 8.83 ($C_{54}H_{58}N_6O_{10}$ requires C 68.20; H 6.15; N 8.84).

5,17-Bis{*N*′-[(4-trifluoromethyl)phenyl]ureido}-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 12

A general procedure was applied to amino derivative **7** (0.10 g, 0.16 mmol) and 4-(trifluoromethyl)phenyl isocyanate (150 mg, 0.11 ml, 0.80 mmol). The first purification was used to remove the majority of carbamate by column chromatography (50 g of Al_2O_3, eluent pure CH_2Cl_2 – carbamate fractions; second eluent pure MeOH – calix[4]arene fractions). The product **12** was finally isolated by preparative GPC (isocratic elution of $CHCl_3$, column PLgel 10 μm, 100 Å, 600 × 25 μm, fl. rate 5 ml min^{-1}, detector UV 254 nm) as a white powder (0.10 g) in 63% yield, mp: 197–199 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ: 8.68 (2H, s, N*H*), 8.05 (2H, s, N*H*), 7.47 (8H, brs, Ar*H*), 7.20–7.12 (6H, m, Ar*H*), 6.93–6.82 (2H, m, Ar*H*), 6.41 (2H, s, Ar*H*), 4.00 (2H, d, J = 12.9 Hz, ArCH_2Ar *ax*), 3.75–3.58 (8H, m, OCH_2 + ArCH_2Ar), 3.43–3.24 (4H, m, OCH_2), 3.08 (2H, d, J = 12.9 Hz, ArCH_2Ar *eq*), 1.81–1.74 (6H, m, OCH$_2$CH_2), 1.41–1.33 (2H, m, OCH$_2$CH_2), 1.04 (6H, t, J = 7.0 Hz, CH_3), 0.82 (3H, t, J = 7.3 Hz, CH_3), 0.66 (3H, t, J = 7.0 Hz, CH_3). ^{19}F NMR (282 MHz, DMSO-d_6, 296 K) δ: −60.49 (6F, s, CF_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 296 K) δ: 157.4, 156.99, 153.6, 153.5, 141.9, 136.7, 135.5, 133.5, 133.4, 130.3, 130.1, 129.3, 126.2 (q, J = 3.8 Hz), 124.7 (q, J = 32.0 Hz), 124.0 (q, J = 271.0 Hz), 123.6, 122.4, 122.1, 118.5, 76.3, 75.4, 75.2, 35.1, 30.3, 24.2, 23.8, 22.5, 10.9, 10.8, 9.3; TOF HRMS (ESI+): calcd for $[C_{56}H_{58}F_6N_4O_6 + Na]^+$: 1019.4159. Found: m/z (rel. int. %) 1019.4153 (100) $[M + Na]^+$.

5,17-Di-*tert*-butyl-11,23-bis[*N*′-(4-nitrophenyl)ureido]-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 13

A general procedure was applied to amino derivative **8** (0.10 g, 0.14 mmol) and 4-nitrophenyl isocyanate (97% purity, 115 mg, 0.68 mmol). The product **13** was isolated by column chromatography (30 g of Al_2O_3, eluent CH_2Cl_2/MeOH = 160 : 1, R_F = 0.15) as a red powder (0.10 g) in 75% yield, mp: 248–250 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 286 K) δ: 9.09 (2H, s, N*H*), 8.30 (2H, s, N*H*), 8.09 (4H, d, J = 9.4 Hz, Ar*H*), 7.54 (4H, d, J = 9.1 Hz, Ar*H*), 7.22 (2H, d, J = 2.3 Hz, Ar*H*), 7.20 (2H, s, Ar*H*), 7.15 (2H, s, Ar*H*), 6.58 (2H, d, J = 2.6 Hz, Ar*H*), 4.04 (2H, d, J = 12.3 Hz, ArCH_2Ar *ax*), 3.78–3.60 (6H, m, OCH_2 + ArCH_2Ar), 3.46–3.32 (4H, m, OCH_2), 3.10 (2H, d, J = 12.9 Hz, ArCH_2Ar *eq*), 2.95 (2H, t, J = 7.5 Hz, OCH_2), 1.83–1.72 (4H, m, OCH$_2$CH_2), 1.50–1.31 (22H, m, OCH$_2$CH_2 + 2 × *Bu*^{t}), 0.99 (6H, t, J = 7.5 Hz, CH_3), 0.63 (3H, t, J = 7.5 Hz, CH_3), 0.54 (3H, t, J = 7.3 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 298 K) δ: 154.9, 153.8, 151.7, 146.7, 144.9, 142.8, 140.8, 135.2, 133.3, 133.2, 133.0, 132.5, 127.5, 125.8, 125.2, 120.2, 118.6, 117.2, 76.0, 74.8, 72.3, 37.8, 34.0, 33.8, 31.7, 31.7, 30.6, 30.0, 23.2, 22.8, 20.6, 10.9,9.6; TOF HRMS (ESI+): calcd for $[C_{62}H_{74}N_6O_{10} + Na]^+$: 1085.5359. Found: m/z (rel. int. %) 1085.5354 (100) $[M + Na]^+$.

5-*tert*-Butyl-11,17,23-tris[*N*′-(4-nitrophenyl)ureido]-25,26,27,28-tetrapropoxycalix[4]arene (*partial cone*) 14

A general procedure was applied to amino derivative **9** (0.10 g, 0.14 mmol) and 4-nitrophenyl isocyanate (97% purity, 183 mg, 1.08 mmol). The product **14** was isolated by column chromatography (30 g of Al_2O_3, eluent CH_2Cl_2/MeOH = 160 : 1, then CH_2Cl_2/MeOH = 1 : 1, R_F = 0.15) as a yellow powder (0.04 g) in 31% yield, mp: 232–235 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ: 9.36 (1H, s, N*H*), 9.00 (2H, s, N*H*), 8.78 (1H, s, N*H*), 8.25 (2H, s, N*H*), 8.20 (2H, d, J = 9.1 Hz, Ar*H*), 8.10 (4H, d, J = 9.1 Hz, Ar*H*), 7.72 (2H, d, J = 9.1 Hz, Ar*H*), 7.49 (4H, d, J = 9.1 Hz, Ar*H*), 7.27 (2H, s, Ar*H*), 7.20 (2H, s, Ar*H*), 7.18 (2H, d, J = 2.6 Hz, Ar*H*), 6.53 (2H, d, J = 2.3 Hz, Ar*H*), 4.03 (2H, d, J = 12.9 Hz, ArCH_2Ar *ax*), 3.77–3.60 (6H, m, OCH_2 + ArCH_2Ar), 3.46–3.32 (6H, m, OCH_2), 3.06 (2H, d, J = 12.9 Hz, ArCH_2Ar *eq*), 1.85–1.73 (4H, m, OCH$_2$CH_2), 1.70–1.62 (2H, m, OCH$_2$CH_2), 1.46–1.36 (11H, m, OCH$_2$CH_2 + *Bu*^{t}) 1.02 (6H, t, J = 7.5 Hz, CH_3), 0.77 (3H, t, J = 7.3 Hz, CH_3), 0.64 (3H, t, J = 7.5 Hz, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K) δ: 155.6, 152.7, 152.2, 152.1, 152.0, 147.3, 147.2, 143.2, 141.5, 141.2, 137.1, 134.1, 133.4, 133.3, 133.2, 132.8, 125.9, 125.7, 121.2, 119.8, 119.0, 118.0, 117.6, 76.5, 75.2, 73.4, 37.7, 34.4, 32.1, 31.0, 23.9, 23.6, 21.2, 11.4, 10.7, 10.2; TOF HRMS (ESI+): calcd for $[C_{65}H_{71}N_9O_{13} + Na]^+$: 1208.5064. Found: m/z (rel. int. %) 1208.5073 (100) $[M + Na]^+$.

Crystallographic measurements

Crystallographic data for $C_{48}H_{62}N_2O_8$ (5). M_r = 795.00, monoclinic system, space group $P2_1/c$, a = 13.7360 (4) Å, b = 17.1360 (5) Å, c = 23.2760 (3) Å, β = 123.9930 (14)°, Z = 4, V = 4542.4 (2) Å^3, D_x = 1.162 Mg m^{-3}, crystal dimensions 0.4 × 0.4 × 0.4 mm. Data were collected on a Nonius KappaCCD diffractometer by monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2) K. An absorption was neglected (μ = 0.08 mm^{-1}) a 47 233 total of measured reflections (θ_{max} = 27.5°), from which 10 398 were unique (R_{int} = 0.033) and 6859 observed ($I > 2\sigma(I)$). The structure was solved by direct methods[16] and refined by full-matrix least squares based on F^2 (SHELXL97).[17] The hydrogen atoms were fixed into idealised positions (riding model) and assigned temperature factors either H_{iso}(H) = 1.2 U_{eq}(pivot atom) or H_{iso}(H) = 1.5 U_{eq}(pivot atom) for –CH$_3$. The refinement converged (Δ/σ_{max} = 0.001) to R = 0.061 for observed reflections and $wR(F^2)$ = 0.196, *GOF* = 1.00 for 533 parameters and all

10 398 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.68, $\Delta\rho_{min}$ −0.49 e Å^{-3}). The displacement parameters of atoms of *tert*-butyl groups are wittnesing disorder of these moieties, however the attempt to split positions of these atoms did not improve the model.

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18 As suggested by one of the referees we have carried out the additional complexation study using the *cone* analogue of receptor **11** to directly compare the complexation abilities of both conformers. As one can see from ESI† (page 14), the complexation of Cl^- occurred with a 1 : 1 stoichiometry (Job plot) and the corresponding complexation constant is 173 ± 24 M^{-1} which is much lower than that of the *partial cone* derivative **11** (1540 ± 370). This indicates that the *partial cone* conformation can be much better choice than the *cone* conformers used so far in the design of novel anion receptors.