A Novel Calix[4]arene-Dipyrrole Conjugate Designed for Complexation of Ion Pairs

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

A novel calixarene derivative with dipyrromethane moieties on the lower rim was prepared. NMR spectroscopy revealed a high selectivity towards sodium cations and the ability to bind ion pairs.

Key words: Calixarenes, Receptors, Ion Pairs

Introduction

Calix[*n*]arenes are a well-known group of macrocyclic oligophenols that are very useful due their unique molecular structures and simple preparation. They are used as important building blocks in supramolecular chemistry, where they have found many applications in the design of sophisticated molecular structures and assemblies. The relatively easy derivatisation of the basic skeleton allows the synthesis of receptors for recognition of anions, cations, neutral molecules, chiral compounds and other substrates [1, 2].

Great attention has been focused on derivatives capable to bind both anions and cations [3a – e]. For such so-called ditopic receptors calix[*n*]arenes [3f – g], (aza)crowns [3h – k], cyclodextrins [3l] and many other scaffolds can be used [3m – 3y]. The aim of this work is to build molecules which could employ the attributes of both calix[4]arenes and oligopyrroles.

It is known from the literature that calix[4]arenes with their *cone* conformation substituted at the lower rim can interact with hard metal cations to form complexes which are very stable both in solution and in the solid state. Among the suitable derivatives we can mention for example different esters [4] and amides [5], and also calixarenes substituted by (oligo)ethylene glycol ethers. Typical examples are represented by calixarenes bearing 2-methoxyethoxy, 2-ethoxyethoxy [4a, 6c] and longer oligoethylene glycol chains [6], as well as a large family of bridged calix-crowns and related compounds [7].

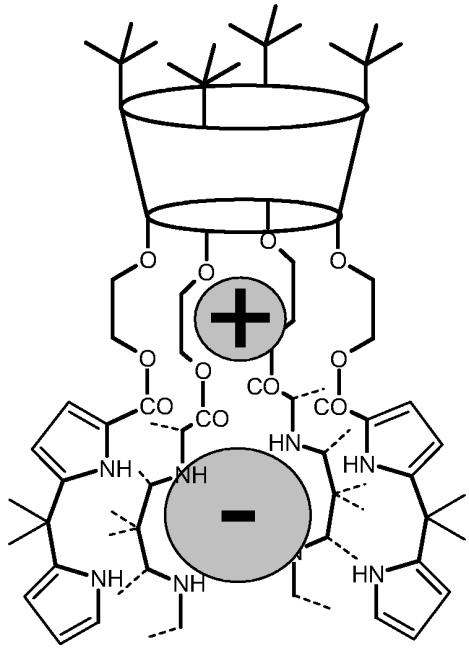
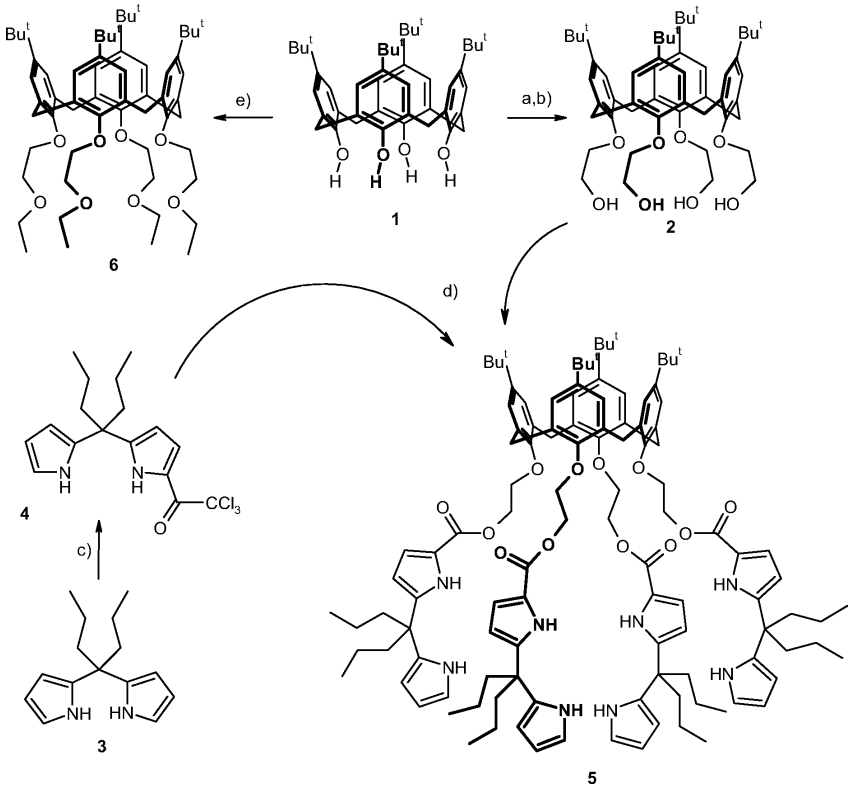


Fig. 1. Design of the target molecule and proposed binding mode (schematically).



Scheme 1. a) $BrCH_2COOEt$, K_2CO_3, acetone, reflux; b) $LiAlH_4$, diethyl ether, r. t.; c) Cl_3CCOCl, Et_3N, heptane, 0 °C; d) Na_2CO_3, phenol, THF, reflux; e) CH_3CH_2-OCH_2CH_2Br, NaH, DMF, r. t.

On the other hand, calix[4]pyrroles [8] and also the corresponding open-chain dipyrroalkanes are very efficient anion receptors [8e, 9]. In previous work [10] we reported the synthesis of reactive derivatives of dipyrroheptane, which can be used for further reactions. One of the possibilities is the appending of dipyrroheptane units to the calix[4]arene skeleton.

Based on this knowledge we designed a molecule for co-operative complexation of both cations and anions, which is schematically depicted in Fig. 1. As the basic building block we used calix[4]arene in the *cone* conformation bearing *tert*-butyl groups on the upper rim to improve the solubility in organic solvents. The lower rim was substituted with four ethylene glycol units, forming a cryptand-like cage that was designed for cation complexation. The ethylene glycol units were terminated by four dipyrrol moieties potentially playing the role of anion receptor.

Results and Discussion

Synthesis

Receptor **5** was prepared according to Scheme 1. The starting calix[4]arene derivative, 5,11,17,23-tetra - *tert* - butyl - 25,26,27,28 - tetrakis(2-hydroxyethoxy)-calix[4]arene (**2**), was synthesised in two steps by (i) alkylation of 5,11,17,23-tetra-*tert*-butyl-calix[4]-arene (**1**) with ethyl bromoacetate, and (ii) reduction of the resulting "tetraacetate" with lithium aluminium hydride [11]. 5-(1-Propyl-1-(pyrrol-2-yl)-butyl)-2-trichloroacetylpyrrole (**4**) was obtained by a modification of the published reaction of 4,4-bis(pyrrol-2-yl)heptane (**3**) and trichloroacetyl chloride [10]. The condensation of derivatives **2** and **4** was achieved by a five day reflux period in THF in the presence of sodium carbonate and phenol. For comparison of complexation abilities, the corresponding model compound without dipyrrolic units, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(2-ethoxyethoxy)calix[4]arene (**6**), was prepared according to the published procedure [4a].

*Complexation study of derivative **5***

Compound **5** was studied by ^1H NMR spectroscopy as a potential receptor for anions, alkali metal cations and also for co-operative and/or simultaneous complexation of ion pairs. All measurements were per-

formed in $CDCl_3/CD_3CN$ 4 : 1 (v/v) solutions at 25 °C. Alkali metal cations were added in the form of well-soluble salts, namely, sodium as the Kobayashi reagent $Na\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$, potassium as the similar salt $K[B(4\text{-}Cl\text{-}C_6H_4)_4]$ and lithium as the picrate. All studied anions were used as the tetra-*n*-butylammonium salts. All titration experiments were performed with constant concentration of receptor (approx. 3×10^{-3} M). The association constants under slow exchange conditions were calculated from concentrations of free ligand, free substrate and complex as determined from integrals in the ^{1}H NMR spectra for several signals. In the case of fast exchange conditions, the association constants were determined from binding isotherms corresponding to 1 : 1 binding using an original non-linear-fitting program [6c] and statistically treated for several signals. To confirm the stoichiometry of the complexes in all cases, job plots were drawn from ^{1}H NMR titration data.

Complexation of anions

The complexation ability toward anions was studied for tetra-*n*-butylammonium chloride, bromide, iodide, hydrogensulphate, dihydrogenphosphate and nitrate. In all cases there were no changes observed in the ^{1}H NMR spectra of receptor **5**. Only after addition of $n\text{Bu}_4\text{N}^+$ HSO_4^-, the colourless solution became pink. The cause of this chromatic change is not known.

Complexation of alkali metal cations

Calixarene-dipyrrole conjugate **5** possesses a very similar structural motif if compared with the tetratosylate of derivative **2**, which was used for the synthesis of the bis-calixarene named calix[4]tube [11]. Both the tetratosylate and the calix[4]tube are known for their pronounced selectivity towards potassium cations over all other alkali metals.

Interestingly, derivative **5** showed no affinity to potassium or lithium, but selectively formed a relatively strong complex with the sodium cation. As the complexation proceeded under slow exchange conditions (^{1}H NMR), the association constant (K_{Na} 5000 M^{-1}) was obtained by integration of the corresponding signals of the NH groups and the $-CH_2-$ bridges of the calixarene framework. The predicted binding mode with sodium being kept inside the cryptand cavity was clearly confirmed by the ^{1}H NMR spectra. Two broadened triplets of the ethylene glycol units (δ = 4.44 and 4.37 ppm) merged into a simple singlet (δ = 4.12 ppm) due to the complexation with sodium. The complexation process is depicted in Fig. 2.

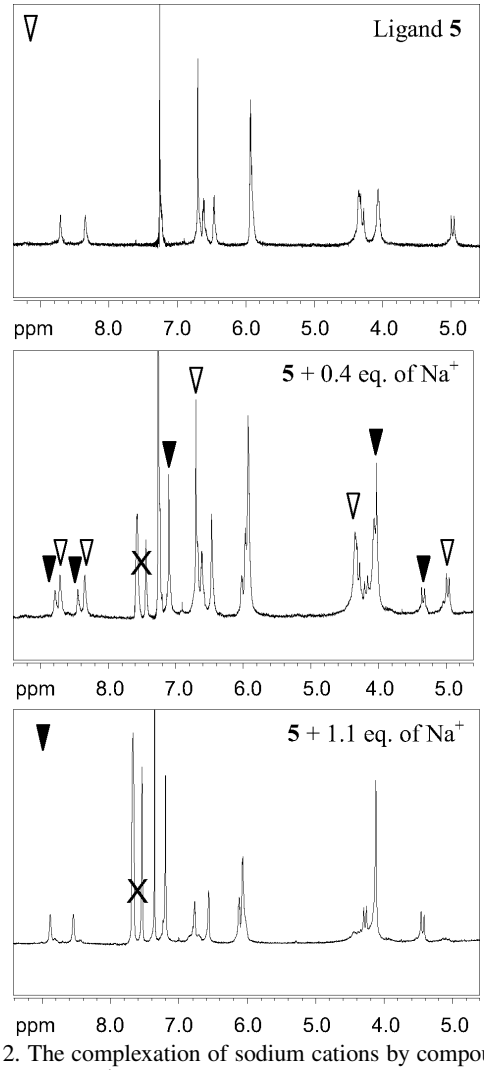


Fig. 2. The complexation of sodium cations by compound **5** as followed by ^{1}H NMR spectroscopy. The white arrow corresponds to the signals of the free ligand **5**, the black arrow to complex **Na·5** and signals of the Kobayashi reagent are marked by a cross.

Complexation of ion pairs

The above-mentioned sodium complex **Na·5** was used for a study of potential co-operative complexation of anions. To a solution of the saturated sodium complex (1.1 eq. of sodium) was added a solution

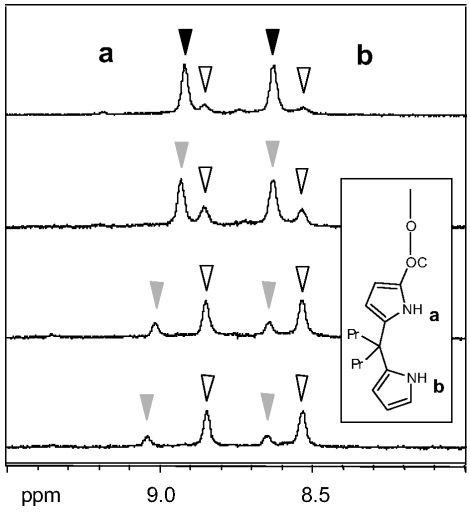


Fig. 3. The complexation of bromide anions by complex **Na·5** as followed by ^{1}H NMR spectroscopy. White arrow: free ligand **5**, black arrow: complex **Na·5**, gray arrow: new species, probably due to the creation of complex **Na·5·Br**.

of a tetra-*n*-butylammonium salt of different halides, namely Cl^-, Br^- and I^-. Titration by $n Bu_4N^+Cl^-$ induced the decomplexation of the sodium cation under slow exchange conditions and precipitation of solid NaCl. Iodide anions induced small changes (< 5 Hz) in the part of the spectrum corresponding to the upper part of molecule **5**, especially in the shifts of the equatorial hydrogen atoms of the $-CH_2-$ bridges, but no changes in the shifts of the NH groups of the pyrrole units.

Really interesting is the behaviour of the **Na·5** complex towards the bromide anion. Addition of $n Bu_4N^+Br^-$ caused two different simultaneous processes: (i) kinetically slow decomplexation of sodium cations and precipitation of NaBr and also (ii) kinetically fast co-operative complexation of the bromide anions by the sodium complex of derivative **5**. The signals of both NH groups in **Na·5** split into two signals. While one of them can be assigned as the signal of the free ligand **5**, the other one does not correspond to the signal of the original complex **Na·5**. The shifts of these NH groups changed after each addition of bromide, which indicated the formation of a new species – probably the complex **Na·5·Br**. Interestingly, after reaching the equilibrium, the ratio between free and bound ligand did not change upon further addition of the bromide salt. The remarkable changes in the signals of the NH-hydrogen atoms during the titration of **Na·5** by $n Bu_4N^+Br^-$ are depicted in Fig. 3. The signals of free ligand **5** are marked by a white arrow (the chemical shift of the NH proton **a** is 8.85 ppm, of proton **b** 8.53 ppm). The black arrow indicate the signals of the NH protons in complex **Na·5**, the grey one illustrates the changes in the new species. While the resonance of the NH proton **a** moved from 8.91 to 9.04 ppm (difference 39 Hz), the induced change for proton **b** is not so remarkable (9 Hz only). The remarkably different behaviour of both NH protons indicates the possible position of the bromide anion within the complex **Na·5·Br**: it is situated closer to the inner cavity formed by the NH-**a** protons, probably because of the electrostatic attraction between the Br^- anion and bound Na^+ cation. Unfortunately, due to these complicated simultaneous processes, the complexation of the bromide anion could not be quantified.

For comparison, we also performed extraction experiments. Solid salt (NaCl, NaBr and NaI, respectively) was added to a solution of ligand **5** ($CDCl_3/CD_3CN$ 4 : 1 v/v) in the NMR tube and the mixture was sonicated overnight. In all cases no change in the ^{1}H NMR spectra of compound **5** was observed. Moreover, extraction from water solution (water saturated with the appropriate sodium salt was shaken with a $CDCl_3$ solution of **5** overnight and the organic phase was measured by NMR) induced no change of shifts in the ^{1}H NMR spectra.

*Complexation study of derivative **6***

The model compound, the tetrakis(2-ethoxyethoxy) derivative **6**, has already been published, but never studied as an alkali metal cation receptor by ^{1}H NMR spectroscopy. Chang *et al.* described the extraction of various picrate salts and transport experiments [4a]. The very similar 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-methoxyethoxy)-calix-[4]arene was also used for extraction of alkali metal salts and as a phase-transfer catalyst [6a].

^{1}H NMR spectroscopy was used only for the complexation studies of other tetrakis(2-ethoxyethoxy) derivatives, that were partly substituted or unsubstituted on the upper rim, $CDCl_3/CD_3OD$ 2 : 1 or 1 : 1 solutions being used [6c].

Our studies of the complexation abilities of derivative **6** towards alkali metal cations and ion pairs were performed under the same conditions as described in the previous part. In contrast to receptor **5**, compound **6** possesses no complexation sites for anions. Hence, direct titrations with tetra-*n*-butylammonium salts were not performed.

Table 1. Association constants of derivatives **5** and **6** towards alkali metal cations K_{as} [M^{-1}].

Ligand	Li^+	Na^+	K^+
5	n.c.	5.000[a]	n. c.
6	12.000	60.000[a]	$> 10^5$

n. c.: no complexation observed (complexation-induced shifts < 5 Hz); [a] slow exchange conditions; estimated errors < 15 %.

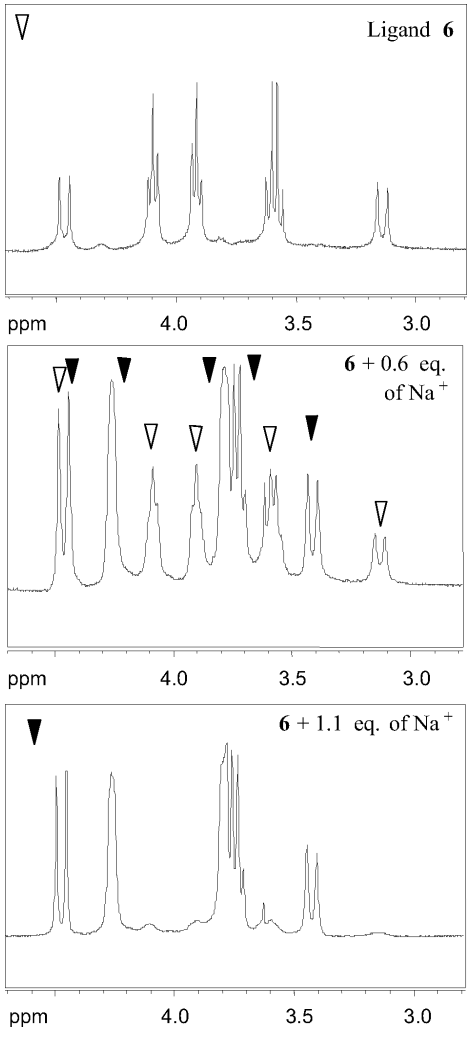


Fig. 4. The complexation of sodium cations by compound **6** as followed by ^{1}H NMR spectroscopy. The white arrow corresponds to the free ligand **6**.

Complexation of alkali metal cations

The study of the complexation abilities of the model compound **6** showed again a different situation for sodium in comparison to the other two studied cations (lithium, potassium): complex **Na·6** was formed under slow exchange conditions, whereas the complexes **Li·6** and **K·6** were formed under fast exchange con-

Table 2. Association constants of alkali metal complexes of derivatives **5** and **6** towards halide anions K_{as} [M^{-1}].

Ligand	Cl^-	Br^-	I^-
Na·5	d.c.	[a]	n. c.
Li·6	200	n.c.	n. c.
Na·6	d.c.	500	n. c.
K·6	d.c.	500	n. c.

d. c.: decomplexation of cation; n. c.: no complexation observed (complexation-induced shifts < 5 Hz); [a] complicated simultaneous processes – see text; estimated errors < 15 %.

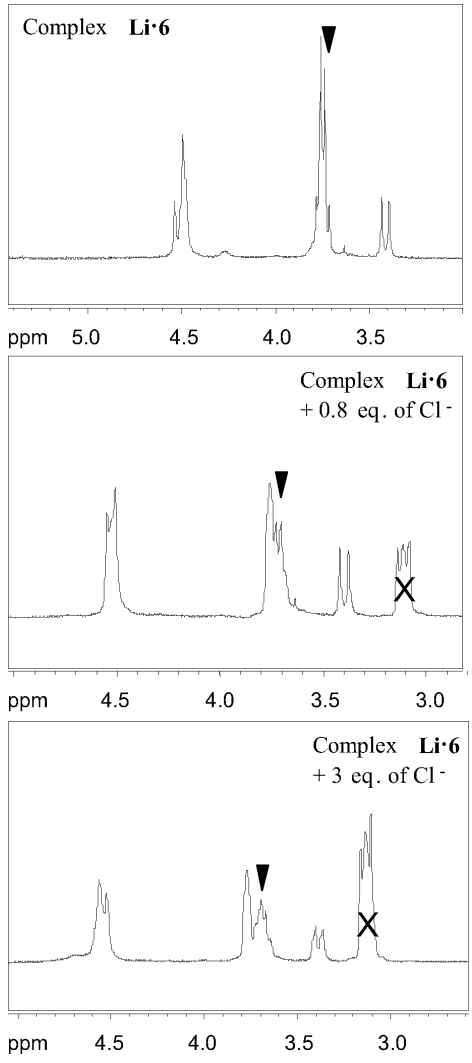


Fig. 5. The complexation of chloride anions by complex **Li·6** as followed by ^{1}H NMR spectroscopy. Black arrow: most significant shift of the O–**CH$_2$**–CH$_3$ signals. The signals of the tetra-*n*-butylammonium cation are marked by a cross.

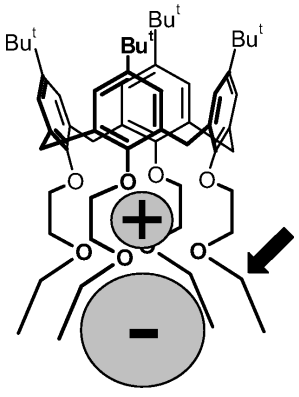


Fig. 6. Proposed binding mode of the ion pair in the complex with ligand **6**.

ditions. The corresponding association constants are summarised in Table 1.

The complexation of sodium cations is depicted in Fig. 4. The ^{1}H NMR spectrum shows two doublets of the CH_2 bridges of the calixarene skeleton (δ = 3.14 and 4.47 ppm) and all signals of three different –CH_2O– groups. The most significant complexation-induced chemical shift (Na^+ cation) was observed for the doublet of the equatorial hydrogen atoms of the CH_2 group ($\Delta\delta$ = 0.27 ppm), whereas the shift of the signal of the axial hydrogen atoms was negligible.

Complexation of ion pairs

Robust complexes of derivative **6** with alkali metal cations were also used for the study of co-operative complexation of halide anions. Results are summarised in Table 2. No complexation of iodide anions was observed, the complexation-induced shifts being < 5 Hz. The chloride anion was co-operatively bound only by **Li·6**. The titration of **Na·6** or **K·6** by nBu$_4$N$^+$Cl$^-$ only caused the decomplexation of the cations. In comparison, **Li·6** did not bind a bromide anion, which was bound by both **Na·6** and **K·6**. The process of co-operative complexation of chloride anions by **Li·6** is depicted in Fig. 5. The largest shifts (up to 20 Hz) were observed for the quartet of the O–CH_2 unit of the terminal ethoxy group, which indicates a binding mode of both cation and anion as depicted in Fig. 6.

Conclusion

A novel calixarene-dipyrrole conjugate **5** was found to be a very selective receptor for the sodium cation. The possibility for co-operative complexation of both cation and anion was confirmed for bromide anions only. However, even in this case anion complexation is accompanied by another competitive process, namely the decomplexation of sodium cations.

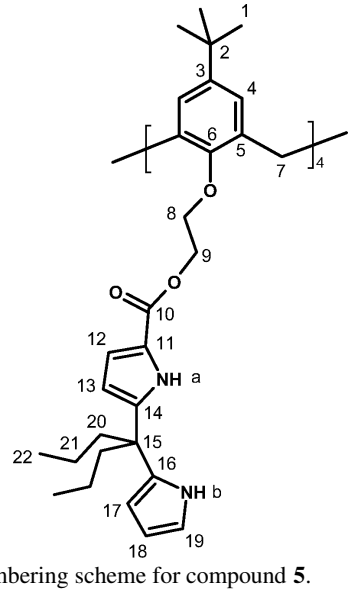


Fig. 7. Numbering scheme for compound **5**.

The study of the model calixarene **6** without dipyrrolic units showed a different complexation of alkali metals cations. The simplest compound has lost the selectivity for sodium and forms strong complexes also with lithium and potassium. Interestingly, only sodium cations are complexed by both receptors **5** and **6** under slow exchange conditions. Receptor **6** without any complexation site for anions, can co-operatively bind bromide and iodide anions after cation complexation.

Experimental Section

Melting points were determined with a Boetius Block apparatus and are uncorrected. ES mass spectra were measured on a Micromass Mattro II instrument. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz, Bruker Avance 300 MHz, and Bruker AMX3 400 spectrometers using tetramethylsilane as an internal standard. For the full assignment of the signals in the ^{1}H NMR and ^{13}C NMR spectra of derivative **5**, gCOSY, gHSQC, gHMBC and 1D NOESY experiments were used.

*5-(1-Propyl-1-(pyrrol-2-yl)-butyl)-2-trichloroacetylpyrrole (**4**)*

A solution of 0.46 g (2 mmol) of dipyrrole **3** and 0.22 g (2 mmol) of triethylamine in 50 mL of heptane was cooled in an ice-bath. Trichloroacetyl chloride (0.36 g, 2 mol) was added and the mixture was stirred at 0 °C for 30 minutes.

Then the solution was poured into 100 mL of water and extracted by 2 × 30 mL of ethyl acetate. The organic layers were collected, washed with 2 × 50 mL of water, dried over magnesium sulphate and evaporated to dryness. The crude product was separated by column chromatography (silica gel, petroleum ether/ethyl acetate 8 : 1) to give 0.56 g (75 %) of derivative **4** (M. p. 98 – 100 °C). – ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.91 (brs, 1 H, NH), 7.80 (brs, 1 H, NH), 7.31 (brs, 1 H, pyrrole β-CH), 6.69 (brs, 1 H, pyrrole α-CH), 6.23, 6.15 and 6.13 (3× brs, 1 H, pyrrole β-CH), 1.98 – 1.90 (m, 4 H, 2 × C–CH_2), 1.15 – 1.10 (m, 4 H, 2 × C–CH_2–CH_2), 0.86 – 0.90 (m, 6 H, 2 × CH_3). – ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 172.9 (carbonyl-C), 148.8, 134.8 and 122.2 (pyrrole α-C), 112.0, 118.0, 110.2, 108.5, and 107.1 (pyrrole-CH), 44.0 (*meso*-C), 40.5 and 17.7 (CH_2), 14.8 (CH_3). – MS-ES: *m/z* = 375.5 (calcd. 375.72 for $C_{17}H_{21}Cl_3N_2O$, $[M]^+$).

*5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-(2-(5-(1-propyl-1-(pyrrol-2-yl)-butyl)pyrrol-2-yl-carbonyloxy)ethoxy)calix[4]arene (**5**)*

150 mg (0.18 mmol) of derivative **2**, 67 mg (0.72 mmol, 4 eq.) of phenol and 285 mg (0.72 mmol, 4 eq.) of 5-(1-propyl-1-(pyrrol-2-yl)-butyl)-2-trichloroacetyl-pyrrole **4** were dissolved in 60 mL of dry THF and 20 mg of Na_2CO_3 was added. The mixture was refluxed for 120 h. After cooling, the mixture was poured into 100 mL of water and extracted with 3 × 30 mL of ethyl acetate. The organic layers were collected, dried over magnesium sulphate and evaporated to dryness. The crude product was separated by column chromatography (silica gel, petroleum ether/ethyl acetate 10 : 1 to remove unreacted **4** and phenol, then the ratio was changed to 4 : 1) to give 96 mg (29 %) of derivative **5** as a pale yellow powder (M. p. 112 – 115 °C). – ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.75 (s, 4 H, NH-a), 8.21 (s, 4 H, NH-b), 6.77 (s, 8 H, ArH), 6.72 (t, *J* = 2.7 Hz, 4 H, H-pyrr-12), 6.56 (m, 4 H, H-pyrr-19), 6.07 – 6.03 (m, 12 H, H-pyrr-13,17 and 18), 4.44 (m, 8 H, 4 × C(O)–O–CH_2), 4.40 (d, *J* = 12.9 Hz, 4 H, ax Ar–CH_2–Ar), 4.17 (m, 8 H, O–CH_2), 3.07 (d, *J* = 12.6 Hz, 4 H, eq Ar–CH_2–Ar), 1.92 – 1.87 (m, 16 H, 8 × C–CH_2), 1.09 (m, 52 H, 4 × *t*Bu + 8 × C–CH_2–CH_2), 0.84 (t, *J* = 6.9 Hz, 24 H, 8 × C–CH_2–CH_2–CH_3). – ^{13}C NMR ($CDCl_3$, TMS, 75 MHz, 25 °C): δ = 161.0 (C-10), 153.2 (C-5), 144.8 (C-3), 143.6 (C-14), 135.7 (C-16), 133.3 (C-6), 125.1 (C-4), 121.2 (C-11), 117.2 (C-19), 116.2 (C-12), 108.3 (C-13), 107.4 (C-17), 105.9 (C-18), 72.4 (C-9), 64.2 (C-8), 43.1 (C-15), 39.7 (C-20), 33.8 (C-2), 31.3 (C-1), 30.9 (C-7), 17.1 (C-21), 14.4 (C-22) (Numbering of carbon and nitrogen atoms according to Fig. 7). – MS-ES: *m/z* = 1873.4 (calcd. 1850.51 for $C_{116}H_{152}N_8O_{12}$, $[M+Na]^+$).

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