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# Novel biscalix[4]arene-based anion receptors

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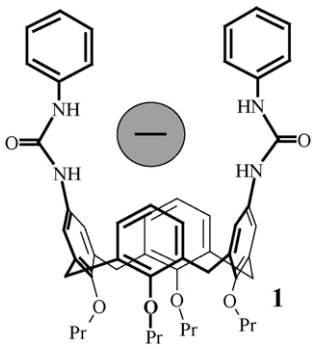
**Abstract**—Novel biscalix[4]arene derivatives where two calixarene units are connected via one or two ureido bridges on the upper rim has been prepared. These compounds represent well preorganised cavities with interesting complexation abilities towards anions. The structure of bis-ureido derivative was proved by X-ray crystallography. 

## 1. Introduction

Calix[4]arenes[1,2] represent macrocyclic compounds widely used in supramolecular chemistry for the construction of various receptors for the complexation of charged or neutral molecules. Their unique three-dimensional structures with almost unlimited derivatisation abilities and a tuneable shape of the molecules make calixarenes ideal candidates for building blocks and/or molecular scaffolds in the design of new more sophisticated molecules.

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Whereas cation complexation has been extensively studied for a long time, the recognition of anions[3] by synthetic receptors based on the calixarenes still remains relatively unexplored. Thus, introduction of activated amides[4] into the upper rim of calixarene derivatives, preorganised in the *cone* conformation, led to the receptors interacting with anions by hydrogen bonds. Other moieties frequently used for anion recognition are urea and thiourea units.[5] As we showed in our previous paper,[6] *cone* or 1,3-*alternate* conformers bearing two urea functions on the upper rim exhibit an interesting complexation ability towards selected anions (halogenides, carboxylates). Our results indicate that the anions are caught by cooperative interactions of both units (compound 1). The bridging of these molecules with an appropriate spacer should lead to receptors with enhanced rigidity (preorganisation) and possibly, to novel complexation properties (selectivity). In this paper we report the synthesis and properties of novel cage compounds based on the bis-calix[4]arenes, possessing preorganised amide or urea moieties in the molecules.

## 2. Results and discussion

### 2.1. Synthesis

The synthesis of bis-calixarenes **6** and **10** was accomplished according to Scheme 1. Starting tetrapropoxycalix[4]arene **2** was mononitrated (product **3**, 45% yield)[7] using 100% $HNO_3$ in dichloromethane/acetic acid mixture and subsequently reduced by $SnCl_2$ in ethanol[8] to give amino derivative **4** in 87% yield. Similar reaction conditions led to 5,17-diaminocalix[4]arene **8** in 26% overall yield. Amino derivatives **4** and **8** were transformed into corresponding isocyanates **5** and **9** by refluxing with triphosgene[8] in toluene. Both compounds were obtained in quantitative yields and due to their alleged instability were used in the next step without further purification. The condensation of aminoderivative **4** with 1 equiv. of isocyanate **5** was carried out in dichloromethane solution at room temperature. Bis-calixarene **6** was obtained in 61% yield after purification by preparative TLC. Analogously, the reaction between difunctional starting compounds **8** and **9** was carried under high dilution conditions by the simultaneous addition of both agents to the big volume of solvent ($CH_2Cl_2$). This method gave cage derivative **10** in 15% yield. Monoamine **4** was also used for the condensation with 1,4-phenylene diisocyanate to form bis-calixarene **11** with two potential complexation sites for anions.

*Keywords*: calixarenes; anion receptors; NMR titration; macrocycles.

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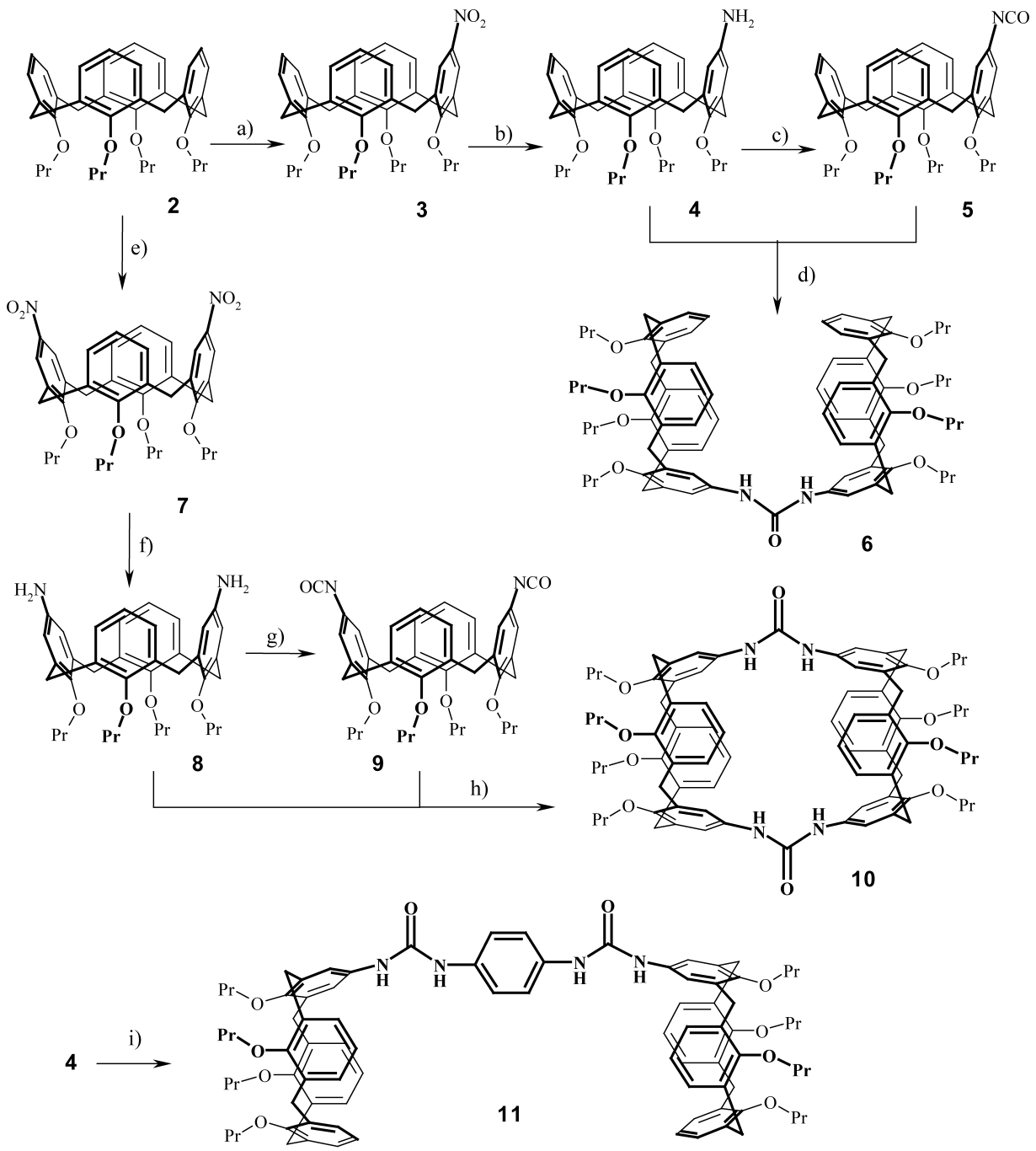
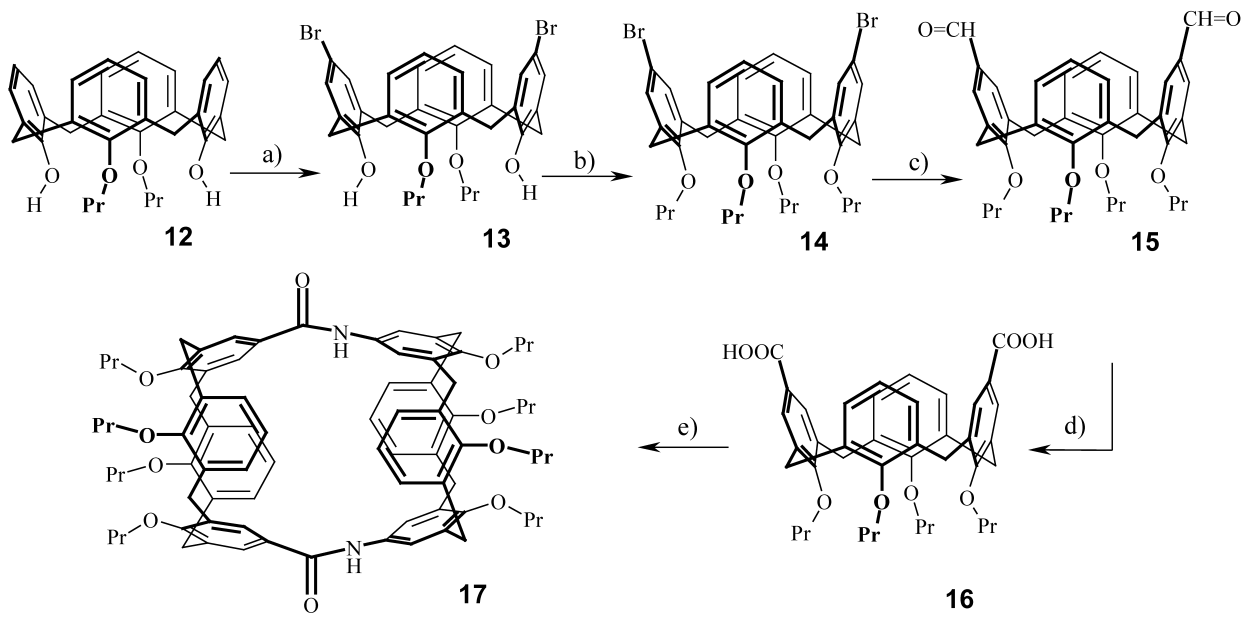



**Scheme 1.** (a) 100% $HNO_3/CH_2Cl_2–CH_3COOH$, rt (45%); (b) $SnCl_2{\cdot}2H_2O$, ethanol, reflux (87%); (c) triphosgene/toluene, reflux (quant.); (d) $CH_2Cl_2$ (61%); (e) 100% $HNO_3/CH_2Cl_2–CH_3COOH$, rt (30%); (f) $SnCl_2{\cdot}2H_2O$, ethanol, reflux (88%); (g) triphosgene/toluene, reflux (quant.); (h) $CH_2Cl_2$/high dilution, rt (15%), (i) 1,4-phenylene diisocyanate/$CH_2Cl_2$, rt 84%).

To evaluate the importance of urea units for the anion binding, derivative **17** bearing two amidic instead of urea functions was prepared according to Scheme 2 in yield 10% under high dilution conditions. Dicarboxylic acid **16** was obtained by the oxidation of corresponding dialdehyde **15** using known procedure.[9]

The $^1H$ NMR spectrum of derivative **10** in $CDCl_3$ consists of very broad signals indicating some additional chemical exchange. The shape of signals is concentration dependent, on the other hand, dynamic $^1H$ NMR methods (+30 to −70°C) did not show any significant changes. More HB-competitive solvent ($CDCl_3/CD_3CN$=4:1 v/v) results in the sharpening of signals, thus supporting the assumption that this phenomenon is caused by intermolecular aggregation based on the HB interactions between urea units. Indeed, the spectrum measured in $CDCl_3$/DMSO-$d_6$=4:1 v/v mixture reflects the high proposed symmetry of this cage derivative: two sets of propyl signals, two doublets of the $CH_2$ bridging group with typical geminal splitting ($J$=13 Hz) and one singlet for the urea NH groups (6.39 ppm). Corresponding $^1H$ NMR spectra of bis-calixarenes **6**, **11** and **17** do not




**Scheme 2.** (a) $Br_2/CHCl_3$, rt (95%); (b) PrI/NaH, DMF, rt (87%); (c) (i) BuLi/THF, −78°C; (ii) DMF; (iii) water (56%); (d) $NaClO_3$/sulfanilic acid, rt (75%); (e) (i) $(COCl)_2/CCl_4$, reflux, (ii) **8**, $CH_2Cl_2$/high dilution, rt (10%).

exhibit similar solvent-dependent behaviour and show typical splitting pattern of monosubstituted and disubstituted calix[4]arenes, respectively.

## 2.2. Complexation study

The complexation ability of compounds **6**, **10**, and **17** was measured by standard $^1$H NMR titration experiments (Table 1) in a $CHCl_3$/DMSO-$d_6$=4:1 v/v mixture (to avoid the self-aggregation of **10**) using a constant calixarene concentration (0.5–1.0 mM) and increasing concentrations of the appropriate anions to obtain different anion/calix ratios (0.1–20). The plot of induced chemical shifts versus anion concentration gave typical titration curves corresponding to the formation of a 1:1 complex. The proposed stoichiometry of the complexation was also confirmed by the measuring of Job plots. The appropriate complexation constant was calculated using original non-linear regression curve-fitting program.[10]

The addition of $C_6H_5COO^-NBu_4^+$ to the solution of **10** (10:1 ratio) leads to high down-field shift of urea –NH– signals (550 Hz) indicating strong interactions with anion. The association constant for benzoate $K$ (734 $mol^{-1}$ l) is almost 20 times higher that that of derivative **6** (43 $mol^{-1}$ l).

**Table 1**. Complexation constants $K_c$ of receptors **6**, **10**, **11** and **17** towards selected anions ($^1$H NMR, $CDCl_3$/DMSO-$d_6$=4:1 v/v, 25°C, 300 MHz)

| Anion | $K_C$ ($mol^{-1}$ l) | | | |
|---|---|---|---|---|
| | **6** | **10** | **11**[a] | **17** |
| $Cl^-$ | 19±3 | 54±5 | 790±295 | –[b] |
| $Br^-$ | –[c] | –[c] | 445±32 | –[b] |
| $I^-$ | –[c] | –[c] | 62±14 | –[b] |
| Benzoate | 43±4 | 734±144 | 1280±735 | –[b] |

[a] Measured in $CDCl_3$.
[b] No changes in NMR observed.
[c] Small induced chemical shifts (<10 Hz).

It clearly shows much better preorganisation of biscalixarene receptor **10** where the cooperative effect of both ureido units is possible. On the other hand, similar derivative **17**, with two amidic functions, does not exhibit any complexation ability towards selected anions (halides, benzoate). Obviously, urea functions are much better anion binding fragments than simple amides, in agreement with our previous finding.[6]

Very interesting size-recognition ability was observed in case of halides. While chloride is complexed by both receptors (54 $mol^{-1}$ l for **10**, 19 $mol^{-1}$ l for **6**), other halides ($F^-$, $Br^-$ and $I^-$) cause only negligible changes of chemical shifts (less than 10 Hz) as a consequence of unsuitable size complementarity of receptors and anions. Similar behaviour (size-dependent recognition of spherical halides) was found in case of biscalixarene **11** ($K_{Cl}$=790 $mol^{-1}$ l, $K_{Br}$=445 $mol^{-1}$ l, $K_I$=62 $mol^{-1}$ l). The ligand **11** was designed to complex two anions at both anion binding positions (urea units), however, the Job plot procedure unambiguously confirmed the exclusive formation of only 1:1 complexes with halides or

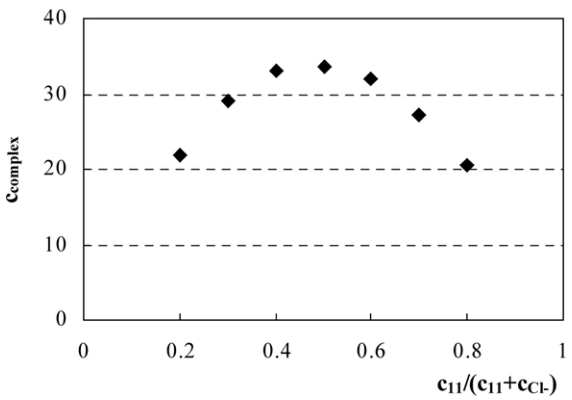



**Figure 1.** Job's plot for **11**/$Bu_4^+Cl^-$ system (300 MHz, $CDCl_3$, $C_{11}$+$C_{Cl^-}$=2 mmol $l^{-1}$).

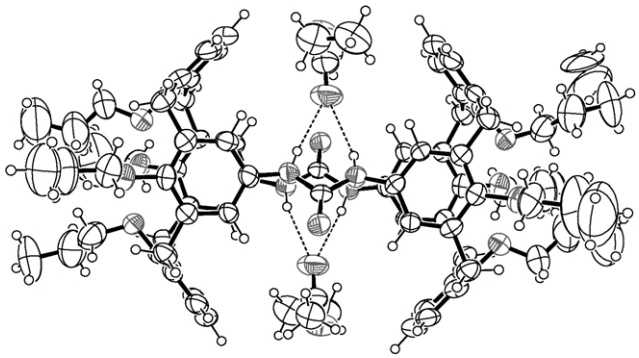


**Figure 2.** ORTEP drawing of the X-ray structure of **10**.

benzoate (Fig. 1). This fact is rather unexpected and the possible explanation may lie in the repulsive interactions between two negatively charged sites in close proximity (particularly in such a non-polar solvent).

### 2.3. X-Ray study

The structure of **10** was unequivocally proven by X-ray crystallography (Fig. 2). Suitable single crystals (monoclinic system, space group $P2_1/a$) were grown from ethyl acetate and they were air-sensitive. Consequently, all operations were carried out in a sealed glass capillary. Both calixarene subunits adopt the *pinched cone* conformation with two opposite aromatic rings pointing out of the cavity and the other two (bearing ureido functions) tilted towards each other. The angles between the main plane defined by the four $CH_2$ groups and the individual aromatic units are approx. 138, 75, 139 and 81°, respectively. Both –NH– groups of ureido units are distorted outside from the cavity what enables the strong hydrogen bonding (H…O distance: 2.19 and 2.28 Å) of the ethyl acetate carbonyl atom (crystallisation solvent) thus forming the 1:2 (**10**/EtOAc) complex.

## 3. Experimental

### 3.1. General

Melting points are uncorrected and were determined using a Boetius Block apparatus. $^1$H NMR spectra were recorded on a Varian Gemini 300 and a Bruker AMX3 400 spectrometers using tetramethyl silane as an internal standard. FAB MS were measured on ZAB-EQ VG Analytical spectrometer. $^1$H NMR titrations were performed with tetrabutylammonium salts of corresponding anions that were dried and stored in evacuated dessicator on $P_2O_5$. Dichloromethane and $CCl_4$ used for the reaction were dried with $CaH_2$ and stored over molecular sieves.

Compounds **3**,[7] **7**,[7] **4**,[8] **5**,[8] **8**,[8] **9**,[8] **13**,[11] **14**,[11] **15**[9] and **16**[9] were prepared according to known procedures.

**3.1.1. Synthesis of derivative 6.** Calix[4]arene **4** (148 mg, 0.25 mmol) was added to the solution of monoisocyanate **5** (158 mg, 0.25 mmol) in 20 ml of dry $CH_2Cl_2$. The reaction mixture was then stirred under nitrogen at room temperature for 1 h. Evaporation of the solvent gave the crude product which was purified by the preparative TLC (silica gel, chloroform/ethyl acetate 100:1) to yield 190 mg of bridged compound **6** (61%) as a white solid. Mp: >350°C (ethyl acetate). $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 6.65–6.75 (m, 12H, H-arom), 6.40–6.50 (m, 6H, H-arom), 6.33 (s, 4H, H-arom), 5.65 (s, 2H, NH), 4.46 (d, 4H, $J$=13.2 Hz, Ar–$CH_2$–Ar, ax.), 4.42 (d, 4H, $J$=13.7 Hz, Ar–$CH_2$–Ar, ax.), 3.82 (m, 16H, –O–$CH_2$–$CH_2$–), 3.16 (d, 4H, $J$=13.2 Hz, Ar–$CH_2$–Ar, eq.), 3.12 (d, 4H, $J$=13.2 Hz, Ar–$CH_2$–Ar, eq.), 1.90 (m, 16H, –$CH_2$–$CH_3$), 0.99 (m, 24H, –$CH_2$–$CH_3$). EA calcd for $C_{81}H_{96}N_2O_9$: C, 78.35; H, 7.79; N, 2.26; Found: C, 78.02; H, 7; N, 2.19. FAB MS $m/z$ (rel. int.) 1241.6 $[M]^+$ (100).

**3.1.2. Synthesis of derivative 10.** The solutions of diaminocalix[4]arene **8** (100 mg, 0.16 mmol) and diisocyanate **9** (108 mg, 0.16 mmol) each in 50 ml of dry $CH_2Cl_2$ were simultaneously added under stirring, over 17 h (syringe pump), into 500 ml of dry $CH_2Cl_2$ (high dilution conditions) under nitrogen atmosphere at room temperature. The mixture was stirred for an additional 7 h and then evaporated to dryness. The crude product was purified by preparative TLC (silica gel, chloroform/acetone 50:1) to yield 30 mg of white crystals of the double bridged compound **10** (15%) as a white solid. Mp: >350°C (ethyl acetate). $^1$H NMR ($CDCl_3$/DMSO-$d_6$ 4:1, 300 MHz) $\delta$: 7.15 (d, 8H, $J$=7.69 Hz, H-arom), 6.93 (t, 4H, $J$=7.14 Hz, H-arom), 6.39 (s, 4H, N–H), 5.82 (s, 8H, H-arom), 4.38 (d, 4H, $J$=13.2 Hz, Ar–$CH_2$–Ar, ax.), 3.99 and 3.59 (2×t, 16H, $J$=7.14 Hz, –O–$CH_2$–$CH_2$–), 3.09 (d, 4H, $J$=13.4 Hz, Ar–$CH_2$–Ar, eq.), 1.84 (m, 16H, –O–$CH_2$–$CH_2$–$CH_3$), 1.01 and 0.86 (2×t, 24H, $J$=7.14 Hz, –$CH_2$–$CH_3$). EA calcd for $C_{82}H_{96}N_4O_{10}$: C, 75.90; H, 7.46; N, 4.32; Found: C, 75.39; H, 7.08; N, 4.12. FAB MS $m/z$ (rel. int.) 1297.3 $[M]^+$ (100).

**3.1.3. Synthesis of derivative 11.** A solution of *p*-phenylene diisocyanate (12 mg, 0.075 mmol) in 30 ml of dry dichloromethane was added dropwise over 0.5 h into the solution of monoamine **4** (100 mg, 0.16 mmol) in 10 ml of dry $CH_2Cl_2$. The reaction mixture was then stirred for 8 h under nitrogen atmosphere and the solvent was evaporated at reduced pressure. The crude residue was purified by preparative TLC (chloroform/acetone 50:1) to yield 87 mg of product **11** (84% yield) as a white solid. Mp: 258°C ($CHCl_3$–MeOH). $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 6.97 (s, 4H, H-arom), 6.80–6.63 (m, 6H, H-arom), 6.21 (br s, 16H, H-arom), 4.35 (d, 8H, Ar–$CH_2$–Ar, ax., $J$=13.5 Hz), 3.86 (m, 8H, –O–$CH_2$–$CH_2$–), 3.65 (m, 8H, –O–$CH_2$–$CH_2$–), 3.06 (d, 4H, Ar–$CH_2$–Ar, eq., $J$=13.2 Hz), 3.04 (d, 4H, Ar–$CH_2$–Ar, eq., $J$=13.5 Hz), 1.84 (m, 16H, –$CH_2$–$CH_3$), 0.97 and 0.85 (2t, 24H, $J$=7.4 Hz). EA calcd for $C_{88}H_{102}N_4O_{10}$: C, 76.83; H, 7.47; N, 4.07; Found: C, 76.25; H, 7.19; N, 3.85. MALDI-TOF MS $m/z$ (rel. int.) 1377 $[M+H]^+$ (100), 1399 $[M+Na]^+$ (79).

**3.1.4. Synthesis of derivative 17.** A mixture of diacid **16** (60 mg, 0.088 mmol) and $(COCl)_2$ (76 μl; 0.88 mmol) in 5 ml of anhydrous $CCl_4$ was stirred under reflux for 3 h. The solvent was distilled off, the residue was dissolved in anhydrous $CCl_4$ (5 ml) and the solvent was again evaporated under reduced pressure. This procedure was repeated twice

to remove all traces of oxalyl chloride. The resulting solid (acyl chloride) was then dried in a high vacuum for 1 h. A solution of the above-obtained acyl chloride (63 mg, 0.088 mmol) in dry dichloromethane (50 ml) and a solution of diaminocalix[4]arene **8** (55 mg, 0.088 mmol) in 50 ml of $CH_2Cl_2$ were simultaneously added under stirring during 6 h (syringe pump) into 500 ml of dry $CH_2Cl_2$ (high dilution conditions) at room temperature under nitrogen atmosphere. The mixture was then stirred for an additional 12 h and evaporated to dryness. The residue was purified by preparative TLC (silica gel, chloroform) to yield 10 mg of product **17** (10%) as a white solid. Mp: >300°C (ethyl acetate). $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.39 (s, 2H, NH), 7.23 (m, 8H, H-arom), 7.05 (m, 4H, H-arom), 6.57 (s, 4H, H-arom), 6.19 (s, 4H, H-arom), 4.42 (m, 8H, Ar–$CH_2$–Ar, ax.), 4.07 (m, 8H, –O–*$CH_2$*–$CH_2$–), 3.61 (m, 8H, –O–*$CH_2$*–$CH_2$–), 3.16 (m, 4H, Ar–$CH_2$–Ar, eq.), 1.81–2.04 (m, 16H, –*$CH_2$*–$CH_3$), 1.08 (m, 12H, –$CH_2$–*$CH_3$*), 0.89 (m, 12H, –$CH_2$–*$CH_3$*). EA calcd for $C_{82}H_{94}N_2O_{10}$: C, 77.69; H, 7.47; N, 2.21; Found: C, 77.15; H, 7.27; N, 2.09. FAB MS *m/z* (rel. int.) 1267.6 $[M]^+$ (100).

### 3.2. Crystallographic study

X-Ray data for $C_{41}H_{48}O_5N_2{\cdot}C_4H_8O_2$ $M$=736.95 g/mol, monoclinic system, space group $P2_1/a$, $a$=19.42(2), $b$=10.54(1), $c$=20.00(1) Å, $\beta$=111.05(6), $Z$=4, $V$=4205(6) Å$^3$, $D_c$=1.16 g cm$^{-3}$, $\mu$ (Cu K$\alpha$)=0.62 mm$^{-1}$, crystal dimensions of 0.8×0.4×0.4 mm. The crystal for data collection was mounted in a glass capillary with mother liquor to prevent desolvation during the analysis. Data were measured at 293 K on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu K$\alpha$ radiation. The structure was solved by direct methods.[12] All heavy atoms were refined anisotropically. The whole structure was refined by full matrix least-squares on $F$ values[13] to final $R$=0.0947 and $R_w$=0.0742 using 3386 independent reflections ($\theta_{max}$=60°). Urea –NH– hydrogen atoms were found from difference Fourier maps and their positions were refined, the other hydrogen atoms were located from expected geometry and were not refined. Psi scan was used for the absorption correction. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 172007. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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