Supporting Information

Inclusion networks of a calix[5]arene-based exoditopic receptor and long-chain alkyldiammonium ions

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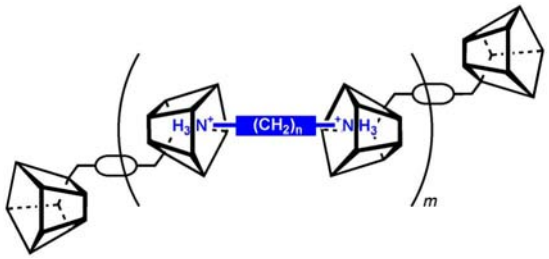

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Experimental Section

General. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Unless otherwise stated, ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$, at 300 and 75 MHz respectively, using TMS as an internal standard. ^{13}C NMR spectra were acquired with the attached proton test (APT) technique. Electrospray ionization mass spectra (ESI MS) were obtained on an Applied Biosystems, Mariner™ ESI TOF quadrupole mass spectrometer. DMF and CH_3CN were dried by standard methods[1] prior to use; other chemicals were reagent grade and were used without further purification. Column chromatography was performed on silica gel (Merck, 230–400 mesh). All reactions were carried out under an argon atmosphere. *p-tert*-Butylcalix[5]arene **1** was synthesized according to a literature procedure.[2]

Compound 2

A suspension of **1** (811 mg, 1.0 mmol) and CsF (760 mg, 5.0 mmol) in DMF (50 mL) was stirred at 50 °C for 1 h and then cooled at rt. α,α'-Dibromo-*p*-xylene (119 mg, 0.5 mmol) in DMF (40 mL) was added dropwise and the resulting mixture was stirred at rt for an additional period of 24 h. Solvent removal under reduced pressure gave a residue which was partitioned between water and CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, and concentrated. The resulting oil was purified by column chromatography (toluene) to afford bis-calixarene **2** in 44% yield. Mp 207–210 °C (CH_3CN/CH_2Cl_2); ^{1}H NMR δ 1.08, 1.22, 1.27 (s, 1:2:2, 90 H), 3.37, 3.41, 3.48 (d, J = 14.1 Hz, 2:1:2, 10 H), 4.03, 4.08, 4.45 (d, J = 14.1 Hz, 1:2:2, 10 H), 5.25 (s, 4 H), 7.13–7.20 (m, 20 H), 7.69, 7.81 (bs, 1:1, 8 H, OH, exchangeable with D_2O), 7.85 (s, 4 H) ppm; ^{13}C NMR δ 30.8, 31.2, 31.36, 31.43, 31.6, 33.84, 33.86, 34.1, 77.2, 125.4, 125.7, 125.8, 126.0, 126.3, 126.42, 126.46, 128.6, 126.9, 132.2, 136.7, 142.6, 143.7, 147.5, 147.6, 149.2, 150.1 ppm; ESI MS, *m/z* 1724 $[M + H]^+$. Anal. Calcd for $C_{118}H_{146}O_{10}$: C, 82.19; H, 8.53. Found: C, 81.95; H, 8.69.

Compound 3

A mixture of **2** (0.604 g, 0.35 mmol), 4-methypentyl tosylate (2.692 g, 10.50 mmol) and anhydrous K_2CO_3 (1.451 g, 10.50 mmol) in CH_3CN (70 mL) was stirred under reflux for 8 days. Excess of base and inorganic salts were collected by filtration and thoroughly washed with CH_2Cl_2. The combined organic layer was concentrated and the residual solid was triturated with MeOH, collected by suction filtration and recrystallized from CH_3CN/CH_2Cl_2 (58% yield). Mp 272–274 °C; ^{1}H NMR δ 0.83, 0.97, 1.19 (s, 1:2:2, 90 H), 0.87, 0.88, 0.93 (d, J = 6.6 Hz, 1:1:2, 48 H), 1.2–1.4 (m, 8 H), 1.48–1.66 (m,

[1] Perrin, D. D.; Armarego, W. L. F. in *Purification of Laboratory Chemicals*, Ed. Pergamon Press, 1989.
[2] Stewart, D. R.; Gutsche, C. D. *Org. Prep. Proced. Int.* **1993**, *25*, 137–139.

16 H), 1.71–1.93 (m, 16 H), 3.18, 3.23, 3.26 (d, J = 13.9 Hz, 2:2:1, 10 H), 3.44–3.54 (m, 8 H), 3.61–3.67 (m, 8 H), 4.51, 4.53, 4.54 (d, J = 13.9 Hz, 2:1:2, 10 H), 4.82 (s, 4 H), 6.70 (s, 4 H), 6.85, 7.08, (pseudo-s, 1:1, 16 H), 7.45 (s, 4 H) ppm; ^{13}C NMR δ 22.75, 22.79, 22.84, 22.9, 28.18, 28.21, 28.23, 28.3, 29.3, 29.7, 31.2, 31.3, 31.5, 33.8, 33.9, 34.0, 35.0, 35.1, 74.0, 74.3, 75.6, 124.8, 125.0, 125.2. 125.9, 126.0, 128.2, 133.60, 133.64, 133.8, 134.05, 134.08, 137.5, 144.45, 144.47, 144.8, 151.8, 152.6, 153.1 ppm; ESI MS, *m/z* 2414.0 $[(M + NH_4)]^+$, 1215.9 $[(M + 2NH_4)]^{2+}$. Anal. Calcd for $C_{166}H_{242}O_{10}$: C, 83.15; H, 10.17. Found: C, 83.52; H, 10.49.

^{1}H NMR complexation experiments

In the titration experiments of bis-calixarene **3** with dipicrates **4** and **5** samples were prepared in the NMR tube by mixing stock solutions of host (3.0×10^{-3} M in $CDCl_3$) and guests (3.6×10^{-2} M in CD_3OD) to a final $CDCl_3/CD_3OD$, (2/1, v/v; 0.750 mL) solvent mixture. Host concentration was kept constant at 2.0×10^{-3} M whereas guest concentration was progressively increased during the experiment (5.0×10^{-4}, 1.0×10^{-3}, 3.0×10^{-3}, 6.0×10^{-3}, and 1.2×10^{-2} M; see traces b–f of Figure 4). Dilution experiments were carried out in $CDCl_3/CD_3OD$ (9/1, v/v). The most concentrated **3**/**5** ($5.0\times10^{-2}/4.5\times10^{-2}$ M/M; trace b of Figure 5) sample was obtained by adding a $CDCl_3$ solution of **3** to a suspension of **5** in CD_3OD, followed by sonication till complete solubilization of the salt. Aliquots of this stock solution were then used to prepare the more diluted **3**/**5** solutions ($1.0\times10^{-2}/9.0\times10^{-3}$, $5.0\times10^{-3}/4.5\times10^{-3}$, $1.0\times10^{-3}/9.0\times10^{-4}$, $5.0\times10^{-4}/4.5\times10^{-4}$ M/M; see traces c–f of Figure 5) employed in the experiments. Spectra were recorded at 300 MHz at 22±1 °C.

Selected ^{1}H NMR data of the various assemblies formed between 3 and 4 or 5

4⊂3 (type A): in $CDCl_3/CD_3OD$ (2/1, v/v) δ –1.83 (br m, β-CH_2, 2 H), –1.12 (br t, α-CH_2, 2 H), –0.64 (br m, γ-CH_2, 2 H), –0.06 (br m, δ-CH_2, 2 H), 0.73 (br m, ε-CH_2, 2 H), 2.85 (t, J = 7.8 Hz, α'-CH_2, 2 H), 4.89, 5.03 (s, XyCH_2, 1:1, 4 H), 6.78 (s, 2 H), 6.92 (pseudo-s, 4 H), 7.04 and 7.10 (AB, J = 2.3 Hz, 4 H), 7.08 (s, 2 H), 7.18 and 7.22 (AB, J = 2.2 Hz, 4 H), 7.33 (d, J = 7.8 Hz, XyH, 2 H), 7.34 and 7.39 (AB, J = 2.2 Hz, 4 H), 7.57 (d, J = 7.8 Hz, XyH, 2 H) ppm.

4⊂3⊃4 (type B): in $CDCl_3/CD_3OD$ (2/1, v/v) δ –1.84 (br m, β-CH_2, 4 H), –1.14 (br t, α-CH_2, 4 H), –0.65 (br m, γ-CH_2, 4 H), –0.06 (br m, δ-CH_2, 4 H), 0.73 (br m, ε-CH_2, 4 H), 2.87 (t, J = 7.8 Hz, α'-CH_2, 4 H), 4. 98 (s, XyCH_2, 4 H), 7.08 (s, 4 H), 7.17 and 7.22 (AB, J = 2.4 Hz, 8 H), 7.34 and 7.38 (AB, J = 2.2 Hz, 8 H), 7.45 (m, XyH, 4 H) ppm.

5⊂3 (type A): in $CDCl_3/CD_3OD$ (9/1, v/v) δ –1.89 (br m, β-CH_2, 2 H), –1.20 (br t, α-CH_2, 2 H), –0.68 (br m, γ-CH_2, 2 H), –0.11 (br m, δ-CH_2, 2 H), 0.68 (br m, ε-CH_2, 2 H), 2.95 (t, J = 7.5 Hz, α'-CH_2, 2 H),

4.87, 4.98 (s, XyCH_2, 1:1, 4 H) ppm.

(3⊃5⊂3)$_m$ (type C, m = 1): in $CDCl_3/CD_3OD$ (2/1, v/v) δ –1.92 (br m, β-CH_2 and β'-CH_2, 4 H), –1.24 (br t, α-CH_2 and α'-CH_2, 4 H), –0.67 (br m, γ-CH_2 and γ'-CH_2, 4 H), –0.22 (br m, δ-CH_2 and δ'-CH_2, 4 H), 0.42 (br m, ε-CH_2 and ε'-CH_2, 4 H), 4.89, 5.03 (s, XyCH_2, 1:1, 8 H), 6.76 (s, 4 H), 6.92 (pseudo-s, 8 H), 7.03 (s, 4 H), 7.05 and 7.10 (AB, J = 2.4 Hz, 8 H), 7.14 and 7.19 (AB, J = 1.8 Hz, 8 H), 7.32 and 7.38 (AB, J = 2.0 Hz, 8 H), 7.33, 7.59 (2×d, J = 7.9 Hz, XyH, 1:1, 4 H) ppm.

5⊂3⊃5 (type B): in $CDCl_3/CD_3OD$ (2/1, v/v) δ –1.86 (br m, β-CH_2, 4 H), –1.14 (bt, α-CH_2, 4 H), –0.65 (br m, γ-CH_2, 4 H), –0.07 (br m, δ-CH_2, 4 H), 0.73 (br m, ε-CH_2, 4 H), 2.91 (t, J = 7.8 Hz, α'-CH_2, 4 H), 5.04 (s, XyCH_2, 4 H), 7.03 (s, 4 H), 7.17 and 7.22 (AB, J = 1.9 Hz, 8 H), 7.34 and 7.42 (AB, J = 2.2 Hz, 8 H), 7.38 (s, XyH, 4 H) ppm.

(3⊃5⊂3)$_m$ (type C, m > 1): in $CDCl_3/CD_3OD$ (9/1, v/v) δ –1.96 (br s, β-CH_2 and β'-CH_2, 4 H), –1.29 (br s, α-CH_2 and α'-CH_2, 4 H), –0.69 (br s, γ-CH_2 and γ'-CH_2, 4 H), –0.26 (br s, δ-CH_2 and δ'-CH_2, 4 H), 0.39 (br s, ε-CH_2 and ε'-CH_2, 4 H), 4.99 (s, XyCH_2, 8 H) ppm.

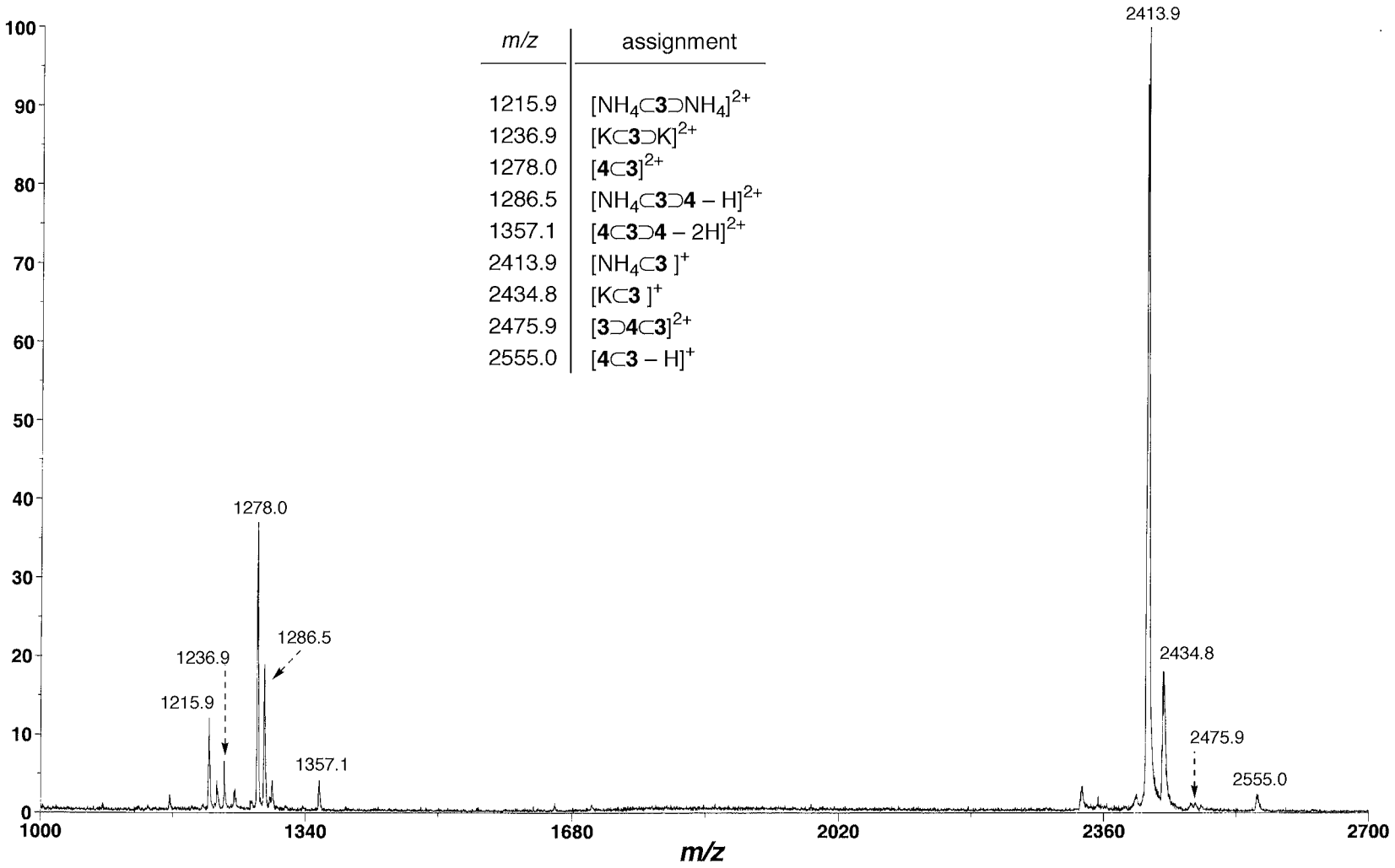

Figure S1. Segment of the ESI MS of an equimolar solution **3** and **4** (7.9×10^{-5} M in $CHCl_3$/MeOH, 2:1).

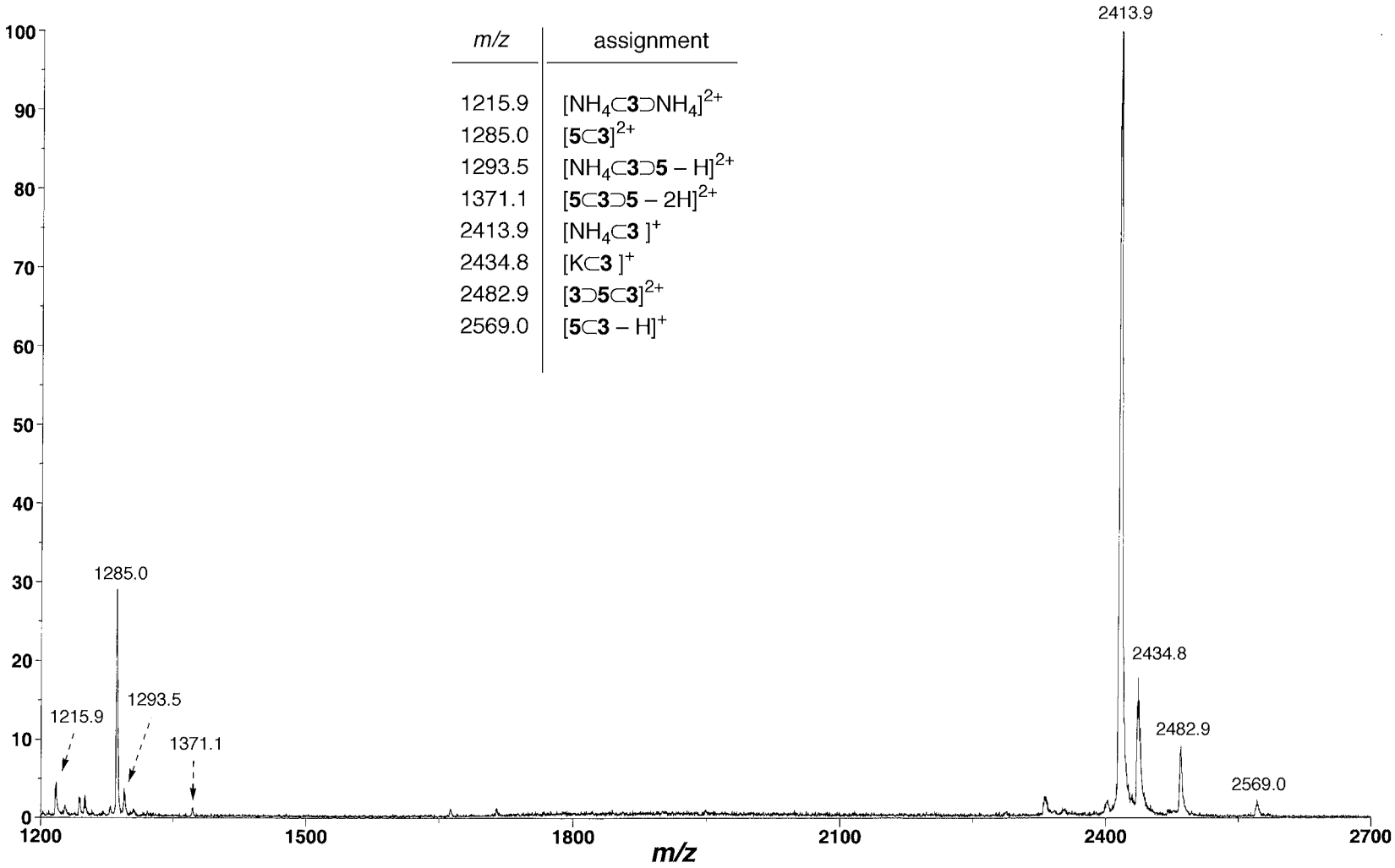

Figure S2. Segment of the ESI MS of an equimolar solution **3** and **5** (7.9×10^{-5} M in $CHCl_3$/MeOH, 2:1).