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Synthesis of New Tren-Based Tris-Macrocycles. Anion Cluster Assembling Inside the Cavity Generated by a Bowl-Shaped Receptor

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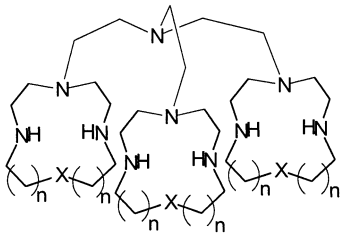
Abstract: The synthesis of three new tris-macrocycles, containing three [12]aneN$_4$ (**L1**), [12]aneN$_3$O (**L2**), or [14]aneN$_4$ (**L3**) moieties appended to a tren unit, is reported. The crystal structure of the $[(Na(ClO_4)_6)\subset \mathbf{L1}_2H_{13}]Na_6Cl_2(ClO_4)_{12}$ compound shows the anionic cluster $[Na(ClO_4)_6]^{5-}$ assembled inside the cavity defined by two bowl-shaped polyammonium receptors, held by multiple charge−charge and hydrogen bond interactions.

Molecular recognition of anionic species by a positively charged synthetic receptor is a field of intense current interest, due to the role played by anions in many biochemical and chemical processes. Polyammonium receptors containing appropriate binding sites and cavities of suitable size and shape have been designed to form selective inclusion complexes with anions.[1−8] Recently, highly charged bowl-shaped polyanionic receptors, derived from sulfonated calix[4,5]arenes, also have been designed to encapsulate positively charged polyammonium macrocycles or metal complexes with crown ethers.[9] Besides preorganization of the binding sites, it is accepted that charge−charge interactions and hydrogen bonding play the major role in the formation of supramolecular complexes between polyammonium receptors and anionic species. Recently, tren-based (tren = tris(aminoethyl)amine) ligands have been used to recognize anionic species, their coordination ability depending on the binding moieties appended to the tren unit.[10−13] In the course of our investigation of the anion binding capabilities of polyammonium macrocycles,[14] we have now designed the new tris-macrocycles **L1**−**L3**. In principle,



n = 1 X = N **L1**
n = 1 X = O **L2**
n = 2 X = N **L3**

these polyamines would give highly charged polyammonium cations at neutral pH, due to the large number of protonatable nitrogen donors. Furthermore, the tren-based structure of these receptors could generate a bowl-shaped cavity of large dimension with C_{3v} symmetry. We hoped that these two structural characteristics could allow the encapsulation of large inorganic anionic substrates or anionic assemblies inside the protonated receptor cavity, through multiple charge−charge and hydrogen bonding interactions.

In this paper we report a general three-step procedure to obtain tren-based polyamine macrocycles. We also report the crystal structure of the $[(Na(ClO_4)_6)\subset \mathbf{L1}_2H_{13}]^{8+}$ cation, which contains the anionic cluster $(Na(ClO_4)_6)^{5-}$ enclosed within the cavity generated by two protonated **L1** receptors.

The procedure developed for synthesis of the tris-macrocycles **L1**−**L3** (Scheme 1) utilizes the simple starting material **1**, which can be obtained by reaction of tris(2-aminoethyl)amine with *N*-tosylated aziridine in high yields.[15] The exasodium salt **2** was obtained by using a standard method. Reaction of the exasodium salt **2** with tosylated diethanolamine **3**,[16] diethylene glicol **4**, or dipropanolamine **5**[17] in 1:3 molar ratio was carried out by using the Richman and Atkins[18] procedure (DMF, 110° C, 6 h) and affords, after purification by column chromatography, the tosylated macrocycles **6**, **7**, and **8**, respectively. Finally, the removal of the tosyl groups was performed in concentrated H_2SO_4 or, in the case of **L2** and **L3**, in HBr/CH_3COOH mixture, since cleavage of ether linkages or propylenic chains takes place in H_2SO_4.

Yields of tosylated derivatives **6**, **7**, and **8** in the critical 1 + 3 cyclization step are reasonably high (15−20%),

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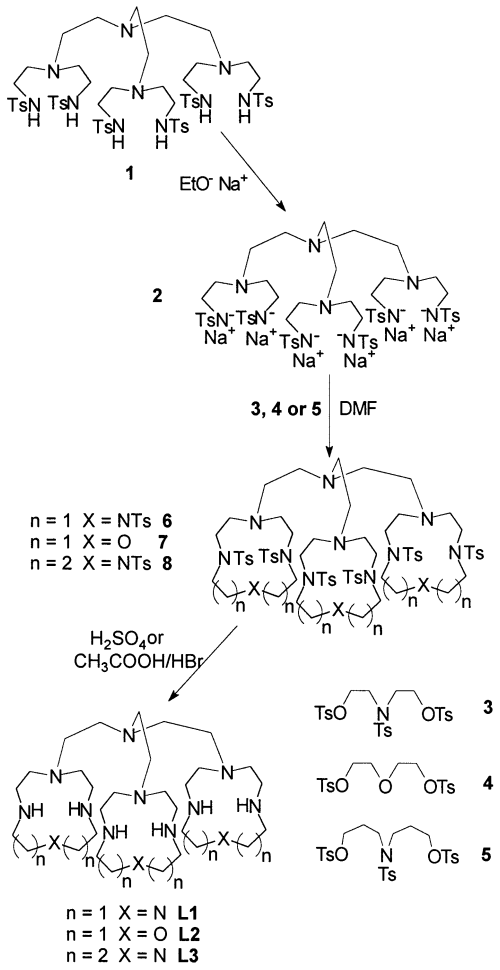
SCHEME 1



considering the strongly competing formation of polymerization or oligomerization products generally observed with this cyclization method.[19,20] These yields still allow considerable quantities of final compounds to be prepared and their chemical properties investigated. Reaction of **2** with **3**, **4**, or **5** was also carried out in boiling CH_3CN in the presence of M_2CO_3 (M = Na, K, or Cs) as base. It has been observed, in fact, that alkaline metal ions may act, depending on their dimension, as templating agents in the cyclization, improving the reaction yield.[19−21] This modification of the Richman and Atkins procedure, however, did not lead to any yield increase, suggesting that no template effect occurs in our case. Although the Richman and Atkins method is a common route to synthesize polyamine macrocycles, our synthetic procedure still represents a simple and versatile three-step route, which can easily be extended to the synthesis of other tailored tris-macrocyclic receptors containing a different number and type of donor atoms or other functional groups, by simple replacement of **3**−**5** in Scheme 1 with opportune reactive fragments.

A potentiometric investigation on the acid−base characteristics of these polyamines points out that highly charged polyammonium cations are formed in aqueous solutions, with the formation of hexa- or eptaprotonated species at neutral pH.[22]

Crystallization of the hydrochloride salt of **L1** at neutral pH in the presence of $NaClO_4$ affords the $[(Na(ClO_4)_6)\subset\mathbf{L1}_2H_{13}]Na_6Cl_2(ClO_4)_{12}$ compound in almost quantitative yield. The low-temperature crystal structure shows that this compound consists of $[(Na(ClO_4)_6)\subset\mathbf{L1}_2H_{13}]^{8+}$ (**9**) supramolecular adducts, Na^+ cations, and Cl^- and ClO_4^- anions. In **9** the cluster of anions $(Na(ClO_4)_6)^{5-}$ is lodged within the cavity defined by two protonated receptors. In $(Na(ClO_4)_6)^{5-}$ the Na^+ cation interacts with six oxygen atoms of different perchlorate anions (Na(1)···O(23) 2.766 Å) and displays a regular octahedral coordination geometry. This coordination environment differs from that found in anhydrous $NaClO_4$, where each Na^+ ion is eight-coordinated by perchorate oxygen atoms, with a distorted square prismatic coordination geometry.[23] Complex **9** shows an overall C_{3v} symmetry, the ternary axis passing through the two N(1) and N(1‴) capped nitrogens of **L1** and the Na^+ ion. Each protonated tris-macrocycle adopts a bowl-shaped conformation. The two receptors are face-to-face coupled, 30° staggered one to each other along the C_3 axis. Such a disposition of the two tris-macrocycles gives rise to an internal cavity where the cluster of anions $(Na(ClO_4)_6)^{5-}$ is assembled (Figure 1), held by charge−charge and hydrogen bonding interactions. Each perchlorate anion, in fact, is lodged among two tetraazamacrocyclic subunits, giving rise to a hydrogen bonding network involving mainly two secondary nitrogens of the two different macrocyclic units (N(5) and N(5″) in Figure 1). At the same time, all four oxygens of the Cl(2) perchlorate are involved in hydrogen bond interactions with the N(4), N(5), and N(5″) nitrogens.

Considering the cocrystallized Na^+, ClO_4^-, and Cl^- ions, the crystal packing gives rise to a particular arrangement of these species, through a series of interactions between the sodium cations and the two different anions. These interactions can be best visualized considering the six sodium cations located at the vertices of a regular octahedron, bridged by ClO_4^- and Cl^- anions. In particular, two different types of perchlorate anions can be recognized. In fact, six perchlorate anions are located at the vertices of the octahedron defined by the sodium ions, each interacting through one oxygen atom with one

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(22) Protonation constants for receptors **L1**−**L3**. **L1**: **L1** + H^+ = **L1**H^+, log K = 10.96(3); **L1**H^+ + H^+ = **L1**H_2^{2+}, log K = 10.20(3); **L1**H_2^{2+} + H^+ = **L1**H_3^{3+} , log K = 9.70(3); **L1**H_3^{3+} + H^+ = **L1**H_4^{4+}, log K = 8.94(9); **L1**H_4^{4+} + H^+ = **L1**H_5^{5+}, log K = 8.97(9); **L1**H_5^{5+} + H^+ = **L1**H_6^{6+}, log K = 8.33(7); **L1**H_6^{6+} + H^+ = **L1**H_7^{7+}, log K = 6.3(1); **L1**H_7^{7+} + H^+ = **L1**H_8^{8+}, log K = 4.1(1). **L2**: **L2** + H^+ = **L2**H^+, log K = 10.10(8); **L2**H^+ + H^+ = **L2**H_2^{2+}, log K = 9.35(8); **L2**H_2^{2+} + H^+ = **L2**H_3^{3+}, log K = 8.9(1); **L2**H_3^{3+} + H^+ = **L2**H_4^{4+}, log K = 8.3(1); **L2**H_4^{4+} + H^+ = **L2**H_5^{5+}, log K = 7.8(1); **L2**H_5^{5+} + H^+ = **L2**H_6^{6+}, log K = 7.6(1); **L2**H_6^{6+} + H^+ = **L2**H_7^{7+}, log K = 5.4(1); **L2**H_7^{7+} + H^+ = **L2**H_8^{8+}, log K = 3.4(1). **L3**: **L3** + H^+ = **L3**H^+, log K = 10.75(4); **L3**H^+ + H^+ = **L3**H_2^{2+}, log K = 10.35(4); **L3**H_2^{2+} + H^+ = **L3**H_3^{3+} , log K = 9.57(6); **L3**H_3^{3+} + H^+ = **L3**H_4^{4+}, log K = 9.51(6); **L3**H_4^{4+} + H^+ = **L3**H_5^{5+}, log K = 8.31(7); **L3**H_5^{5+} + H^+ = **L3**H_6^{6+}, log K = 8.21(6); **L3**H_6^{6+} + H^+ = **L3**H_7^{7+}, log K = 7.06(1); **L3**H_7^{7+} + H^+ = **L3**H_8^{8+}, log K = 6.75(1); **L3**H_8^{8+} + $2H^+$ = **L3**H_{10}^{10+}, log K = 11.7(1); **L3**H_{10}^{10+} + H^+ = **L3**H_{11}^{11+}, log K = 4.04(1). The protonation constants were determined in 0.1 M NaCl at 298.1 K, using the method and procedure described in ref 14.

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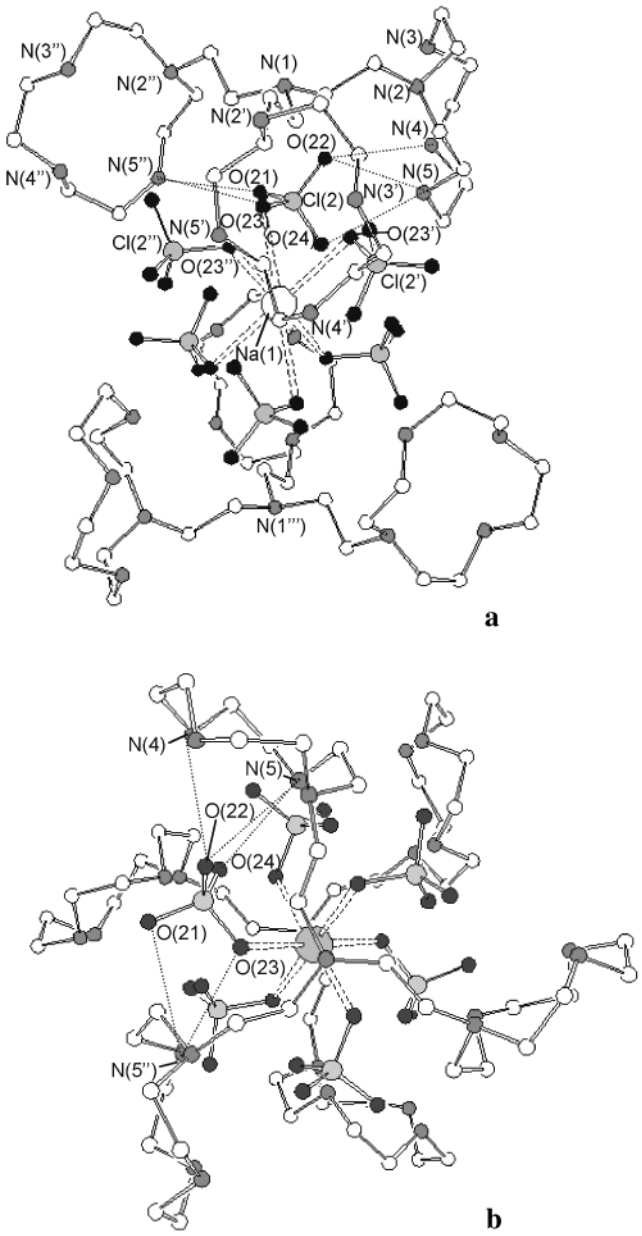

FIGURE 1. Side view (a) and top view (b) of the crystal structure of **9**. Hydrogen bond interactions involving the Cl(2) perchlorate: N(5)···O(22), 3.173(3) Å; N(5)···O(24), 3.456(2) Å; N(4)···O(22), 3.3.173(3) Å; N(5′)···O21 3.323(3) Å; N(5′)···O(22), 2.932(2) Å. The hydrogen bond interactions involving the other symmetry-related five-perchlorate anions are not shown for clarity.

Na^+ cation. The remaining perchlorate anions are lodged above the six faces of the octahedron, each interacting with three Na^+ cations. Finally, the remaining two opposite faces of the octahedron are occupied by two chloride anions, each interacting with three Na^+ cations. A view of this unit, herein indicated by **10**, is reported within the Supporting Information.

Although **10** cannot be considered a defined anionic species and its assembly is simple due to the crystal packing, it can be helpful to visualize the rather complicated hydrogen bond network involving **9** and the external Cl^- and ClO_4^- anions. **9** and **10**, in fact, can be considered associated via strong hydrogen bonds between

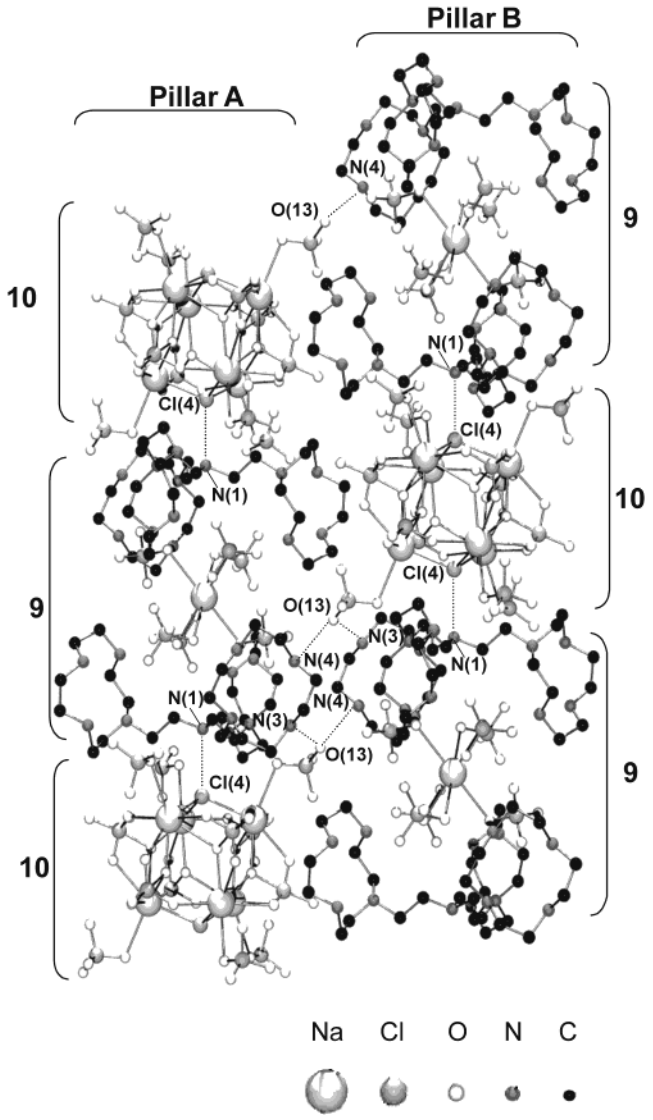

FIGURE 2. Crystal packing of the $[(Na(ClO_4)_6)\subset \mathbf{L1}_2H_{13}]Na_6Cl_2(ClO_4)_{12}$ compound, displaying two adjacent pillars (A and B) associated via hydrogen bond interactions (O(13)···N(4)). The hydrogen bond interactions between **9** and **10** belonging to the same cluster are also shown (Cl(4)···N(1), O(13)···N(3)).

the N(1) nitrogen of **9** and the chloride anion of **10** (N(1)···Cl(4) 3.005 Å) and between the N(3) nitrogens and the perchlorate anions at the vertices of the octahedral cluster **10** (N(3)···O(13) 2.916 Å). As a consequence, the crystal lattice can be visualized as composed of infinite pillars of closely packed alternate **9** and **10** units (Figure 2).

Although the ΔF Fourier map does not allow us to localize the acidic protons in the **9** adduct, the involvement of N(5) in several hydrogen bonds with the perchlorate of the encapsulated $(Na(ClO_4)_6)^{5-}$ cluster and the presence of rather strong interactions between N(1) and N(3) with the chloride and perchlorate anions of the **10** moiety strongly suggest that these amine groups are the receptor protonation sites in **9**.

Each pillar interacts via hydrogen bonding with three adjacent symmetry-related pillars to give an infinite columnar structure. A couple of interacting pillars are depicted in Figure 2, which shows the hydrogen bond

interactions between the perchlorate anions at the vertices of **10** of one of the pillars and the N(4) nitrogen of a tetraazamacrocyclic moiety of the adjacent pillar. This hydrogen bond interaction, however, is weaker (O(13)···N(4) 3.292 Å) than those previously observed for N(1) and N(3) with perchlorate oxygens.

However, the most interesting finding still remains the encapsulation of $(Na(ClO_4)_6)^{5-}$ in the cavity generated by two protonated **L1** receptors. In fact, although examples of the crystal structure of inorganic anions encapsulated inside macrocyclic cavities have been reported recently,[24,25] this is the first case of an organized cluster of anions assembled within the cavity generated by polyammonium receptors.

Experimental Section

General. Compound **1** was obtained (84% yield) by reaction of tri(2-aminoethyl)amine with 6 equiv of *n*-tosylaziridine, according to a previously reported method.[15] 1,4,7-Tritosyl-1,4,7-triazaeptane **3**[16] and 1,5,8-tritosyl-1,5,9-triazanonane **5**[17] were prepared as already reported. 1,7-Ditosyl-1,4,7-trioxaeptane **4** was obtained commercially. ^{1}H and ^{13}C NMR spectra were recorded on a 300-MHz instrument. CF-FAB mass spectra were performed with a VG-7070EQ mass spectrometer. The mass spectra of **L1**, **L2**, and **L3** were performed on the "free" amines obtained by extraction with $CHCl_3$ of alkaline solutions containing their hydrobromide or hydrochloride salts.

Tris(2-(1,4,7-tri(*p*-tolysulfonyl)-1,4,7,10-tetraazacyclododecane)ethyl)amine (6). All reactions were carried out in a nitrogen atmosphere. A solution of sodium ethanolate, obtained by addition of small bits (ca. 200 mg each) of sodium (5.2 g, 0.22 mol) in dry ethanol (250 cm^3), was added to a hot solution of compound **1** (50 g, 0.037 mol) in dry ethanol (150 cm ^{3}). The resulting suspension was refluxed for about 30 min and then the solvent was evaporated under reduced pressure to give the sodium salt **2** as a white solid. This was dissolved in dry DMF (500 cm^3) and K_2CO_3 (80 g, 0.58 mol) was added. To the resulting suspension, heated at 110 °C, was added **3** (76.8 g, 0.11 mol) in 500 cm^3 of dry DMF under stirring over a period of about 3 h. The reaction mixture was kept at 110 °C for 12 h and then evaporated to 150 cm^3. The suspension was then poured into a 1-dm^3 water−ice mixture with mechanical stirring. The crude compound was filtered off, washed several times with water, and dried in a vacuum. The product **6** was chromatographed over a silica gel column (400 g, 4-cm diameter) with a 100:0.8 CH_2Cl_2:MeOH mixture. The eluted fractions were collected and evaporated to dryness to yield compound **6** as a white solid (10 g, 14%). Mp 254−257 °C. ^{13}C NMR ($CDCl_3$) δ (ppm) 21.96, 49.51, 51.54, 51.74, 52.50, 52.74, 56.18, 127.87, 128.06, 130.17, 135.16, 136.32, 143.89. Anal. Calcd for $C_{93}H_{123}N_{13}O_{18}S_9$: C, 56.0; H, 6.2; N, 9.2. Found: C, 55.86; H, 6.20; N, 9.11.

Tris(2-(1,4,7,10-tetraazacyclododecane)ethyl)amine Dodecahydrochloride (L1·12HCl). Compound **6** (5 g, 0.0025 mol) was dissolved in 20 cm^3 of 96% H_2SO_4 and the resulting solution was kept at 100 °C for 72 h. The solution was cooled and added dropwise to 200 mL of diethyl ether, with stirring, to give a thick oil that was separated and washed twice with diethyl ether. The residue was dissolved in a minimum amount of water and the solution was eluted through an ionic exchange resin (Dowex, 1 × 8, anionic form). The solution containing the free amine was vacuum evaporated to dryness to afford a yellowish oil, which was dissolved in dry ethanol. HCl (37%) was added dropwise until the complete precipitation of a white solid, which was filtered off, washed with ethanol, and dried in a vacuum (2.8 g, 80%). **L1**·12HCl: ^{1}H NMR (D_2O, pH 8.3) δ (ppm) 2.78 (12H, m), 2.93 (24H, m), 3.11 (24H, m); ^{13}C NMR (D_2O, pH 8.3) δ (ppm) 42.43, 42.93, 44.98, 48.97, 49.78, 50.15. MS *m*/*z* 612 ([M + H]$^+$). Anal. Calcd for $C_{30}H_{81}N_{13}Cl_{12}$: C, 34.33; H, 7.78; N, 17.35. Found: C, 34.53; H, 7.81; N, 17.82.

Tris(2-(4,10-(*p*-tolysulfonyl)-7-oxa-1,4,10-triazacyclododecane)ethyl)amine (7). This compound was synthesized from **1** (47.9 g, 0.036 mol) and **4** (56 g, 0.108 mol) following the procedure reported for **6**. The product was purified by column chromatography eluting with 100:3 CH_2Cl_2:MeOH. Yield 11.2 g, 20%. Mp 234−237 °C. ^{13}C NMR (25 °C, $CDCl_3$) δ (ppm) 21.82, 48.30, 49.55, 52.90, 53.51, 54.40, 70.90, 127.39, 130.05, 136.71, 143.57. Anal. Calcd for $C_{72}H_{102}N_{10}O_{15}S_6$: C, 56.1; H, 6.7; N, 9.1. Found: C, 56.15; H, 6.67; N, 9.09.

Tris(2-(7-oxa-1,4,10-triazacyclododecane)ethyl)amine Octahydrobromide (L2·8HBr). Hexatosylated compound **7** (8 g, 0.0052 mol) and phenol (45 g, 0.48 mol) were dissolved in 33% HBr/CH_3COOH (430 mL). The solution was stirred at 90 °C for 22 h. The resulting suspension was filtered and the solid residue washed several times with CH_2Cl_2. The yellowish solid was recrystallized from a 1:2 water/ethanol mixture to give **L2** as its octahydrobromide salt (5.3 g, 81%).

L2·8HBr: ^{1}H NMR (D_2O, pH 2) δ (ppm) 3.04 (12H, t), 3.16 (6H, t), 3.39 (12H, t), 3.44 (12H, t), 3.56 (6H, t), 3.96 (12H, t). ^{13}C NMR (D_2O, pH 2) δ (ppm) 44.90, 47.48, 47.83, 49.82, 51.81, 65.92. MS *m*/*z* 618 ([M + H]$^+$). Anal. Calcd for $C_{30}H_{76}N_{10}O_3Br_8$: C, 28.73; H, 5.30; N, 11.17. Found: C, 28.71; H, 5.27; N, 11.10.

Tris(2-(1,4,8,12-(*p*-tolysulfonyl)-1,4,8,12-tetraazacyclododecane)ethyl)amine (8). 8 was synthesized from **1** (29.2 g, 0.022 mol) and **5** (40 g, 0.065 mol) following the procedure reported for **6**. The product was purified by column cromatography eluting with a 100:0.5 $CHCl_3$:MeOH. Yield 8.5 g, 18%. Mp 208−211 °C. ^{13}C NMR (25 °C, $CDCl_3$) δ (ppm) 21.88, 29.96, 47.97, 53.69, 54.71, 127.68, 130.26, 135.96, 136.5, 143.76, 143.86. Anal. Calcd for $C_{72}H_{102}N_{10}O_{15}S_6$: C, 57.06; H, 6.52; N, 8.74. Found: C, 57.37; H, 6.78; N, 8.92.

Tris(2-(1,4,8,12-tetraazacyclododecane)ethyl)amine Undecahydrobromide (L3·11HBr). This compound was synthesized from **8** (4.5 g, 0.0021 mol) following the procedure reported for **L2**. **L3**·11HBr: ^{1}H NMR (D_2O, pH 2) δ (ppm) 2.25 (12H, q), 3.05 (12H, t), 3.19 (6H, m), 3.32 (36H, m), 3.60 (6H, m).^{13}C NMR (D_2O, pH 11) δ (ppm) 21.98, 43.63, 43.47, 44.91, 48.93, 49.05, 52.53. MS *m*/*z* 697 ([M + H]$^+$). Anal. Calcd for $C_{36}H_{92}N_{13}Br_{11}$: C, 27.26; H, 5.85; N, 11.48. Found: C, 27.54; H, 6.02; N, 11.64.

X-ray Structure Analysis. $C_{60}H_{120}N_{26}O_{72}Cl_{20}Na_7$, MW 3227.76, trigonal, space group $R\bar{3}$, a = 21.670(2) Å, b = 21.670(2) Å, c = 23.534(2) Å, V = 9570(1) Å^3, Z = 3. Single-crystal X-ray structure analysis was carried out on a crystal of dimensions 0.30 × 0.30 × 1.00 mm^3 using a CCD SMART 1K diffractometer with gobel mirror monochromated Cu Kα (λ = 1.54178 Å) radiation at 100 K. Data collection to $2\theta_{max}$ of 115.9° gave 9707 reflections collected. The structure was solved by the direct method of the Sir-97 program. Refinement was performed by means of the full-matrix least-squares method of the SHELX-97 program. Refinement included 289 parameters on 2603 unique reflections for which $I > 2.00\sigma(I)$), to give R = 0.083, R_w = 0.234, and GOF = 0.972. As is common in perchlorate, the six perchlorate anions at the face of the octahedron defined by the six sodium ions in **9** exhibited disorder (five oxygen peaks, two given 33% and 66% occupancy, respectively).

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Supporting Information Available: Drawing of **10**, tables of crystallographic and experimental data, complete atomic positional parameters, anisotropic temperature factors, and bond distances and angles for $[(Na(ClO_4)_6)\subset\mathbf{L1}_2H_{13}][Na_6Cl_2(ClO_4)_{12}]$; ^{13}C NMR spectra for **6**, **7**, and **8**, and ^{1}H and ^{13}C NMR spectra of **L1**, **L2**, and **L3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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