Formation of Discrete, Functional Assemblies and Informational Polymers through the Hydrogen-Bonding Preferences of Calixarene Aryl and Sulfonyl Tetraureas

Ronald K. Castellano[†,‡] and Julius Rebek, Jr.*[,‡]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and The Skaggs Institute for Chemical Biology and Department of Chemistry, The Scripps Research Institute, La Jolla, California 92037

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Abstract: Derivatives of the calix[4]arenes in the cone conformation featuring either aryl urea or sulfonyl urea functions on their larger (upper) rims dimerize through hydrogen bonding to give molecular capsules. The capsules act as hosts that reversibly bind smaller molecule guests in organic media. Heterodimers form when both aryl and sulfonyl ureas are present, and the heterodimers form *exclusively* with respect to the homodimers. The heterodimerization encodes *information* at the molecular level and allows the predictable formation of discrete aggregates of nanometer dimensions. Evidence for the reversible assembly of these structures is provided by ^{1}H NMR, guest encapsulation studies, and gel permeation chromatography. Covalent attachment of these calixarene aryl and sulfonyl ureas at their smaller (lower) rims leads to polymeric assemblies in which the informational content is preserved.

Introduction

Calixarenes with urea functions attached to their larger (upper) rims dimerize reversibly in organic solvents and create capsules (**1·1**, Figure 1).[1−3] This dimerization is driven by the formation of intermolecular hydrogen bonds between urea functions in a cyclic "head-to-tail" arrangement. Small-molecule guests of suitable size and shape (e.g., benzene, camphor) are reversibly encapsulated in these host spaces on a time scale that is slow in NMR spectroscopic measurements. Covalent attachment of two calixarene subunits at their smaller (lower) rims leads to the formation of functional polymeric capsules, or polycaps.[4]

It has been observed that homodimeric capsules of aryl urea derivatives (**1a·1a**, Figure 2) and homodimeric capsules of sulfonyl urea derivatives[3a] (**1b·1b**) disproportionate to form heterodimers (**1a·1b**, hereinafter referred to as **2**) exclusively.[5] Two reasons for this preference come to mind. First, the increased acidity of the sulfonyl urea −NH proton[6] complements the relative basicity of the aryl urea. Additionally, and perhaps more significantly, a NOESY spectrum of **2** (see the Supporting Information) shows NOE contacts between the aryl groups of both ureas in the heterodimer. These aryl−aryl interactions are apparently stabilizing, since corresponding structures bearing alkyl ureas show less than 10% heterodimerization with sulfonyl urea partners.[7] Whatever the cause, the selective dimerization represents encoded *information* at the molecular level. We report here the consequences of this information in the formation of discrete molecular assemblies of nanometer dimensions[8] and those of a larger and polymeric scale.[9]

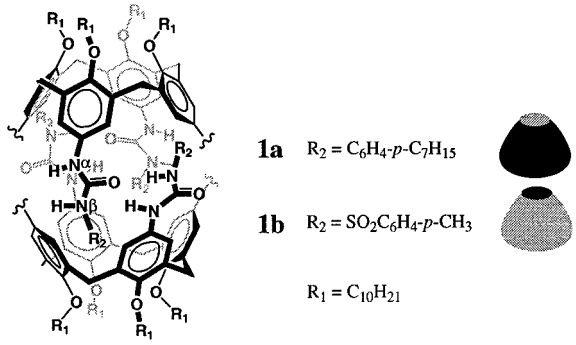

Figure 1. Calix[4]arene tetraurea derivatives dimerize through hydrogen bonds in a "head-to-tail" fashion to form capsules **1·1**. (Some of the ureas have been omitted in the structure for clarity.)

Results and Discussion

Formation of Discrete Assemblies. When the polycap species **3a**[4] (Figure 3) is treated with a stoichiometric amount

* Address correspondence to this author at The Scripps Research Institute.
† Massachusetts Institute of Technology.
‡ The Scripps Research Institute.

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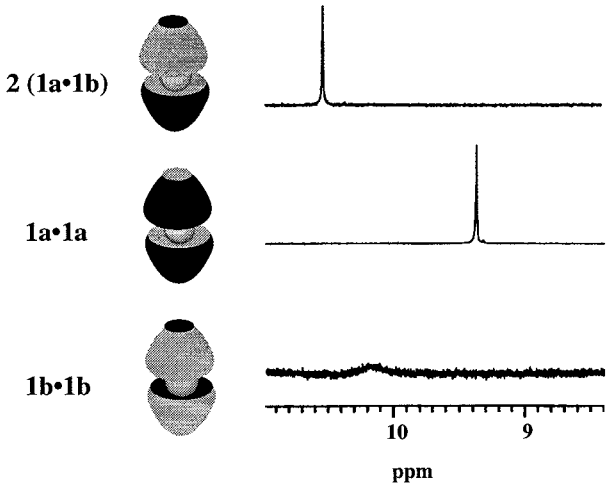

Figure 2. Combination of aryl urea homodimer **1a·1a** and sulfonyl urea derivative **1b·1b** gives exclusive formation of the corresponding heterodimer **2** (all dimers shown with encapsulated solvent guest). Only the downfield portions of the ^{1}H NMR spectra in $CDCl_3$ are shown.

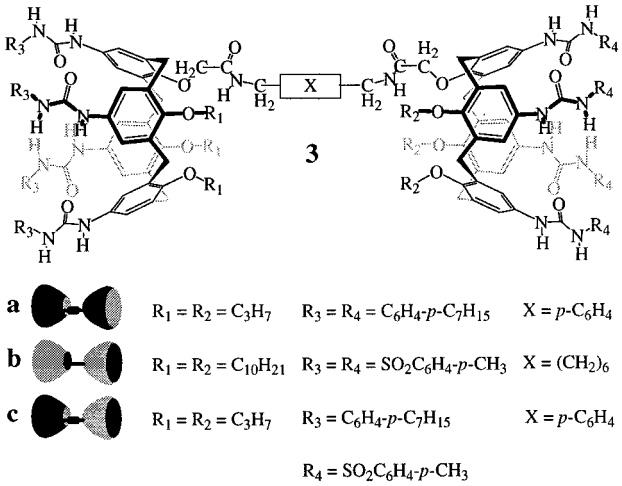

Figure 3. Covalent attachment of two tetraurea calixarenes at their lower rims gives new bifunctional subunits. These reversibly form polymeric capsules or discrete assemblies with their complements in solution.

of sulfonyl urea **1b**[5] in $CDCl_3$, the "dumbbell" system **4** (Figure 4) emerges. The assembly process occurs rapidly and is complete within minutes of mixing. The ^{1}H NMR spectrum shows four singlets at low field corresponding to the four different $-N_\beta H$ (Figure 1) protons of the sulfonyl urea portion that caps the system.[10] At first glance, only two singlets might

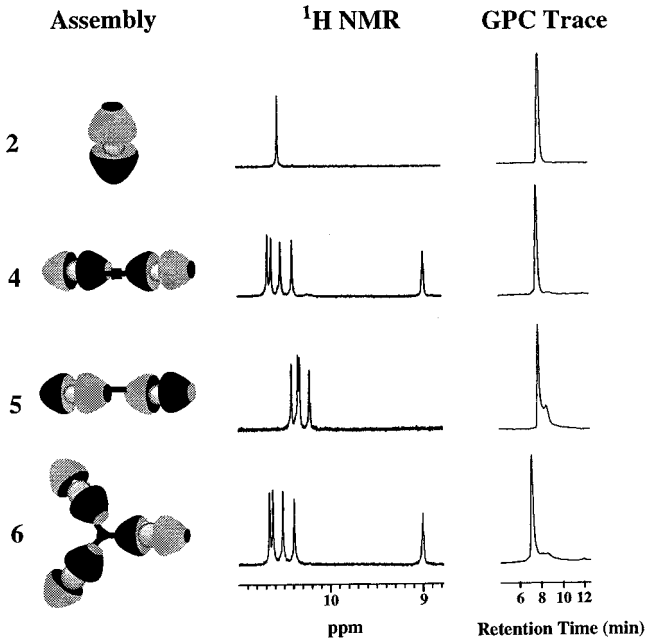

Figure 4. Structures **2** and **4**−**6** form as well-defined, discrete assemblies in $CDCl_3$. The heterodimerization of aryl ureas with sulfonyl ureas drives the assembly and the sharp traces observed in GPC analysis suggest stable species.

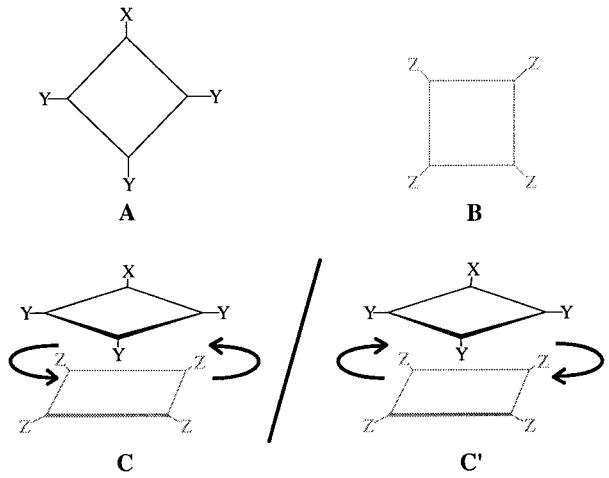

Figure 5. Graphical depiction of the symmetry associated with assemblies **4**−**6**.

be anticipated from the symmetry of the assembly, but a closer look reveals that the situation is more complicated. Certainly, the centerpiece of the "dumbbell", e.g. **3a**, as a monomeric species should (and does) show three signals for the $-N_\beta H$ urea protons that reflect the structure's plane of symmetry (depicted as A in Figure 5, where three of the four substituents are equivalent). Likewise, monomeric **1b** shows one signal for these protons (depicted as B in Figure 5, where all substituents are equivalent). Upon assembly into a "dumbbell," a sense of directionality in the urea functions is introduced: the "head-to-tail" arrangements of the ureas can be clockwise or counterclockwise, giving rise to cycloenantiomers[11] (C and C′) of

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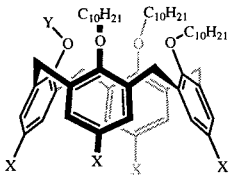
(10) These assignments are based on NOESY and ROESY spectra of **2**. See the Supporting Information for details.

Scheme 1



7 X = t-Bu Y = H

$BrCH_2CO_2Et$, NaH, DMF

8 X = t-Bu Y = CH_2CO_2Et

HNO_3, CH_3CO_2H

9 X = NO_2 Y = CH_2CO_2Et

H_2, Ra Ni (cat), toluene

10 X = NH_2 Y = CH_2CO_2Et

OCN-SO_2-C_6H_4-*p*-CH_3, CH_2Cl_2

11 X = NHCONH-SO_2-C_6H_4-*p*-CH_3 Y = CH_2CO_2Et

LiOH, THF/H_2O

12 X = NHCONH-SO_2-C_6H_4-*p*-CH_3 Y = CH_2CO_2H

the complex. When these pictorial representations are applied to the analysis of **4**−**6,** it becomes apparent that each urea in these assemblies is in a magnetically inequivalent environment, and a total of 16 urea protons can be observed in their respective ^{1}H NMR spectra (eight from the centerpiece and eight from the caps).[12] The peak at 9 ppm arises from the amide −NH resonance of the central spacer where X = *p*-C_6H_4 (Figure 3).

Through synthetic methods similar to those devised for **3a**, the bis(tetrasulfonyl urea) **3b** was prepared (Scheme 1). Phenol **7** was prepared from the parent *p-tert*-butylcalix[4]arene via alkylation with 1-iododecane using a procedure described by Shinkai and co-workers.[13] Subsequent alkylation with ethyl bromoacetate, nitration, and reduction yielded the tetraamine **10**. Treatment of the amine with *p*-toluenesulfonyl isocyanate followed by saponification of the ethyl ester gave the versatile intermediate acid **12**. Finally, coupling of 2 equiv of the acid to 1,8-diaminooctane using PyBOP[14] provided **3b** in good yield. Addition of 2 equiv of **1a** to this polymeric species gives the inverted "dumbbell" **5** (Figure 4), in which the central sulfonyl ureas are capped by aryl ureas. Again, no other species can be detected in the ^{1}H NMR spectrum.

More complicated systems follow in two-dimensional assemblies, as in **6** (Figure 4). The components of this system are derived from 1,3,5-triethynylbenzene **13**, which was made through known acetylene coupling chemistry from 1,3,5-tribromobenzene.[15] Subsequent coupling to ethyl 4-iodobenzoate (Scheme 2) using Sonogashira's conditions[16] gave the corresponding triester **14**, which was then saponified to afford the rigid, C_3-symmetric triacid **15**. The calixarene subunit of **6** was prepared as shown in Scheme 3. The previously described monoacid **16**[4] was coupled to mono-BOC-protected *p*-xylylenediamine[17] with PyBOP to give **17**. Deprotection with HCl(g) gave the amine salt **18**, which was subsequently coupled to the

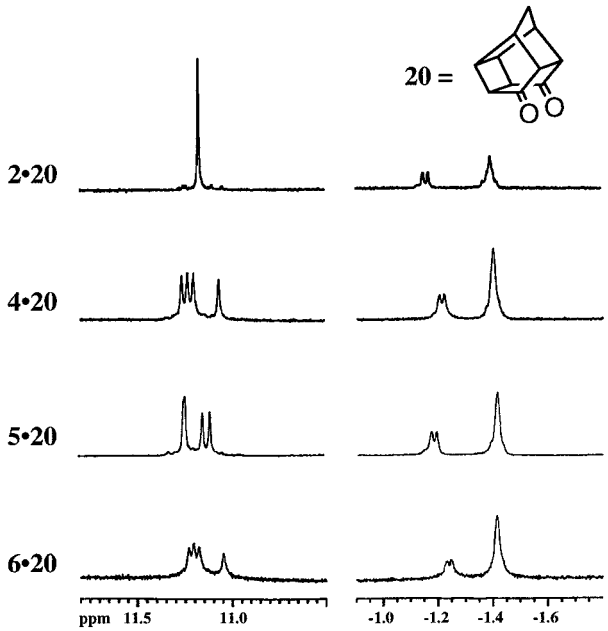
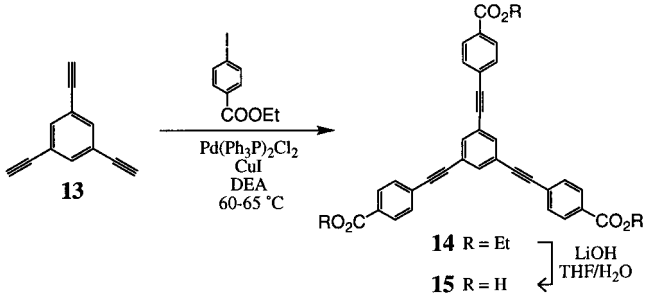


Figure 6. Discrete assemblies **2** and **4**−**6** encapsulate a polycyclic guest **20**. Their ^{1}H NMR spectra in *p*-xylene-d_{10} show the expected $-N_\beta H$ resonances at low field and several strongly shielded resonances from the encapsulated guest.

Scheme 2



triacid **15** to give the complete centerpiece of assembly **6**, shown in Scheme 3 as **19**. Addition of $CDCl_3$ to this compound produces an uncharacterized insoluble gel, presumably through the formation of cross-linked polycaps. In contact with aromatic solvents such as benzene and *p*-xylene, it exists as an insoluble powder. Nonetheless, sonication of **1b** with the gel in $CDCl_3$ yields a homogeneous solution, and the capped derivative **6** emerges as the only species detectable by ^{1}H NMR (Figure 4). Again the characteristic four signals for the $-N_\beta H$ protons of the cap are observed.

Further Characterization: Guest Encapsulation and GPC Analysis. Functional characterization of these systems involved the study of their guest encapsulation behavior, and physical characterization was possible through the use of gel permeation chromatography (GPC) analysis. Addition of the pentacyclic dione **20** (Figure 6) to solutions of **2** and **4**−**6** in *p*-xylene-d_{10} shows upfield encapsulated guest resonances by ^{1}H NMR. In all cases the anticipated stoichiometry of the guest is observed, i.e. one guest molecule for **2**, two for either **4** or **5**, etc. Assembly **6** is the most complex, as it is comprised of four molecules as the host species and three guest molecules.

Whitesides and co-workers have introduced the application of GPC in the characterization of discrete hydrogen-bonded

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(12) The spectra of **4**−**6** in Figure 4 are quite sharp although they represent diastereomers of the complexes which differ by the clockwise/counterclockwise array of the ureas on their ends. Apparently this level of information is not communicated between the ends of the assemblies.

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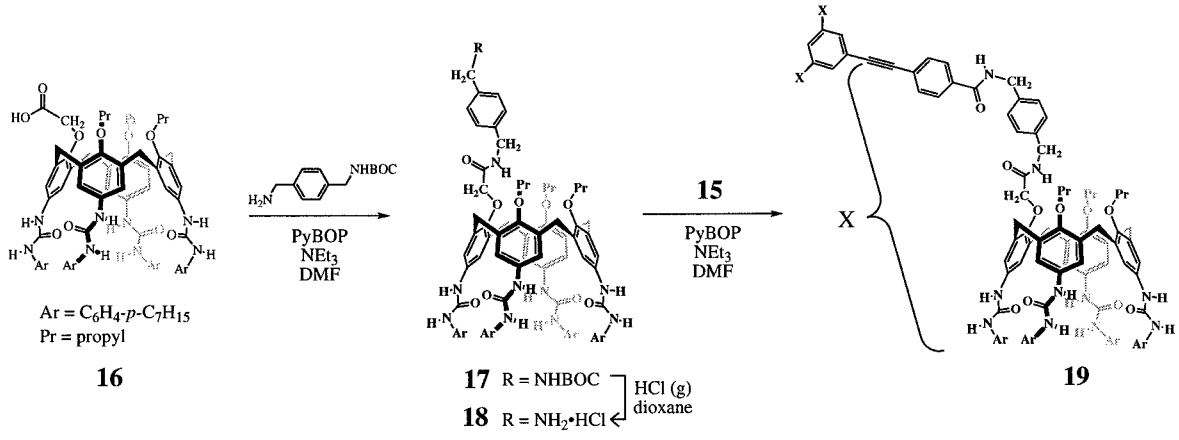
Scheme 3



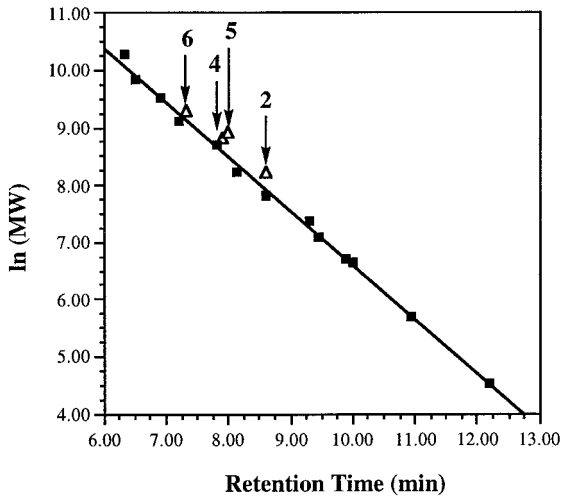


Figure 7. Linear correlation between molecular weight and retention time is observed for a variety of standards (filled squares). Assemblies **2** and **4**−**6** deviate slightly from the calibration line due, in part, to differences in shape and functional groups.

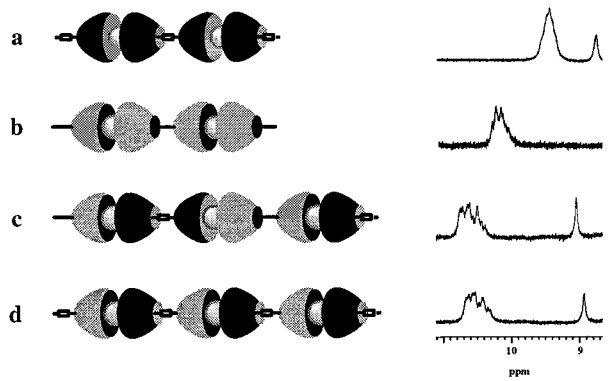


Figure 8. Aryl urea polycaps (a) and sulfonyl urea polycaps (b) in $CDCl_3$ disproportionate to give alternating subunits (c). The self-complementary subunit **3c** in $CDCl_3$ assembles as polycaps of predictable "head-to-tail" sequence (d). Only the downfield portion of the ^{1}H NMR spectra in $CDCl_3$ is shown.

complexes.[8] This method offers information regarding aggregate stability and, in some cases, molecular weight. Structures **2** and **4**−**6** give sharp GPC traces (Figure 4) in $CHCl_3$ reflecting their relative stability versus, for example, dimers **1a·1a** and **1b·1b**, which offer broader traces (see the Supporting Information). To correlate retention time with molecular weight, a standardization curve (Figure 7) was obtained from eight polystyrene standards, three monomeric calixarene derivatives, and two substituted benzenes (see the Supporting Information for structures). Although assemblies **2** and **4**−**6** fall slightly off the calibration line, their homology makes their retention times reliably consistent and gives further evidence for the assignment of structure.[18]

"Smart" Polymers. The information offered by the aryl urea−sulfonyl urea heterodimerization can be used for programmed, or "smart" polymers (Figure 8). As previously reported,[4] calixarene **3a** forms linear polycaps in organic solvents (Figure 8a), as does **3b** (Figure 8b). Representative ^{1}H NMR spectra show the $-N_\beta H$ protons of each clustered around 9.4 and 10.2 ppm, respectively. The heterodimerization tendency of aryl and sulfonyl ureas predicts that a combination of **3a,b** should lead to polycaps of alternating subunits. Figure 8c shows the result of the experiment; indeed, only $-N_\beta H$ resonances from the aryl urea−sulfonyl urea interaction are observed in the ^{1}H NMR spectrum clustered around 10.6 ppm. Likewise, the self-complementary derivative, **3c**, is expected to polymerize "head-to-tail" with alternating aryl urea and sulfonyl urea rims. This system was prepared from combination of amine **18** with acid **22** (=**12** with propyl rather than decyl chains on the lower rim). Acid **22** was made from its corresponding ethyl ester **21**, available in one step from the known tetraamine.[4] Polycaps do in fact form in this system (Figure 8d), and the spectrum closely resembles that of the alternating **3a·3b** (Figure 8c). Again, no telltale signals for capsules of the aryl urea−aryl urea neighbors are detectable by ^{1}H NMR. Unfortunately, GPC studies on these systems are less reliable as their molecular weights exceed the exclusion limit of the GPC column.[19]

Outlook. The preference of the aryl urea−sufonyl urea associations represents information in the sense of a binary code. As such, it suggests a new type of informational polymer that differs from those found in nature. We will report on the development of such systems in due course.

(18) Differences in both shape and functional groups from the standards make the rentention times of assemblies **2** and **4**−**6** necessarily deviate from the standard calibration line. These assemblies are, however, similar to each other in these regards, making molecular weight estimations reasonable, although only in a comparative sense (see ref 8).

(19) The exclusion limit of the column used is ≈30 kDa (based on polystyrene standards), which corresponds to a retention time on the order of 6.3 min. Beyond this point there no longer exists a linear correlation between molecular weight and retention time. All of the polymeric systems investigated have retention times below this limit, thereby precluding molecular weight assignments. Additionally, polycap traces tended to be prohibitively broad, preventing even direct comparison to polystyrene standards.

Experimental Section

General. All chemicals were used without further purification unless otherwise specified. Proton (^{1}H) NMR spectra were recorded on Bruker DRX-600 (600 MHz) or AM-300 (300 MHz) spectrometers. Carbon (^{13}C) spectra were recorded on a Bruker DRX-600 (151 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer Paragon 1000PC FT-IR spectrometer. The fast atom bombardment (FAB) positive ion mass spectra were obtained on a VG ZAB-VSE double-focusing high-resolution mass spectrometer equipped with a cesium ion gun. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry experiments were performed on a PerSeptive Biosystems Voyager-Elite mass spectrometer with delayed extraction. Electrospray ionization (ESI) mass spectrometry experiments were performed on an API III Perkin-Elmer SCIEX triple-quadrupole mass spectrometer. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were passed through columns of activated aluminum oxide as described by Grubbs and co-workers[20] prior to use.

GPC Measurements. GPC measurements were performed using a TosoHaas (Montgomeryville, PA) G3000-HHR column (no. 17355) equipped with a HHR-L guard column (no. 17368). HPLC-grade chloroform was purchased from Aldrich Chemical Co. and used without further purification. The column was connected to a Waters HPLC system equipped with a 717 autosampler, 600 controller, and 996 photodiode array (PDA) detector. GPC traces are shown within the wavelength range 245−265 nm. Representative samples were injected with toluene as a standard (retention time in $CHCl_3$ = 12.2 min). Retention times given for **2** and **4**−**6** are the average of three to five runs. All polystyrene standards were purchased from Aldrich Chemical Co. with the exception of MW 5970 and 9100, which were purchased from TosoHaas.

5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(decyloxy)-28-hydroxycalix[4]arene (7).[13] A 500-mL round-bottomed flask was charged with the parent *p-tert*-butylcalixarene (10.0 g, 15.4 mmol), $Ba(OH)_2{\cdot}8H_2O$ (17 g, 54 mmol), BaO (16 g, 24 mmol), and DMF (200 mL). The alkylating agent, 1-iododecane (100 mL, 462 mmol), was then added, and the resulting mixture was vigorously stirred at room temperature. After 24 h, TLC (70:1 hexanes/EtOAc) revealed a complex mixture. The DMF was removed in vacuo, and the remaining residue was partitioned between $CHCl_3$ (300 mL) and water (300 mL) and stirred for several minutes. The organic layer was separated, washed with water (500 mL), dried over $MgSO_4$, and filtered. Concentration of the filtrate gave the product as a solution in excess 1-iododecane. This solution was added directly to an SiO_2 column (800 mL) to remove the excess reagent (hexanes → 70:1 hexanes/EtOAc). All fractions containing the desired product (R_f = 0.3) were combined and concentrated to a yellow oil. The oil was again subjected to SiO_2 chromatography (70:1 Hex/EtOAc, 1200 mL). Fractions containing only the desired product were combined and evaporated to give the pure product as a viscous, pale yellow oil (9.65 g, 59%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (s, 2H), 7.05 (s, 2H), 6.52 (d, 2H, J = 2.3 Hz), 6.51 (d, 2H, J = 2.4 Hz), 5.72 (s, 1H), 4.37 (d, 2H, J = 12.6 Hz), 4.33 (d, 2H, J = 13.1 Hz), 3.89 (m, 2H), 3.78 (m, 4H), 3.23 (d, 2H, J = 13.2 Hz), 3.16 (d, 2H, J = 12.6 Hz), 2.30 (m, 2H), 1.98−1.84 (m, 4H), 1.37−1.18 (m, 42H), 1.33 (s, 9H), 1.33 (s, 9H), 0.90−0.88 (m, 9 H), 0.83 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 154.14, 151.95, 150.86, 145.51, 145.06, 141.35, 136.11, 132.34, 132.00, 129.45, 125.64, 125.01, 124.80, 124.70, 76.34, 74.87, 34.02, 33.73, 33.55, 31.93, 31.86, 31.67, 31.59, 31.50, 31.25, 31.03, 30.97, 30.23, 29.99, 29.75, 29.64, 29.62, 29.40, 29.28, 26.24, 26.16, 22.64, 22.60, 22.55, 14.01; IR (thin film) 3545, 2956, 2924, 2854, 1483, 1467, 1362, 1202, 871 cm^{-1}; HRMS (FAB; M + Cs^+) calcd for $C_{74}H_{116}O_4$Cs 1201.7928, found 1201.7997.

5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(decyloxy)-28-[(ethoxycarbonyl)methoxy]calix[4]arene (8). The alcohol **7** was suspended in anhydrous DMF (20 mL) and THF (80 mL) under N_2 prior to the addition of 1.3 g (31 mmol) of NaH (60% dispersion in mineral oil). The mixture was heated to 50 °C for 1 h to effect complete deprotonation. To the cloudy mixture was added ethyl bromoacetate (3.5 mL, 31 mmol), and stirring was continued at the above temperature for 14 h. Most of the solvent was removed in vacuo, and the residue was dissolved in $CHCl_3$ (200 mL). The organic layer was washed with 1 M HCl (250 mL) and water (250 mL) and dried over $MgSO_4$. Following filtration and concentration, the resulting oil was dried under high vacuum. The oil was dissolved in a minimum amount of 60:1 hexanes/EtOAc and added to a SiO_2 column (800 mL) and eluted with 50:1 hexanes/EtOAc (R_f = 0.36). The desired product (8.0 g, 88%) was isolated as a clear, colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.90 (s, 2H), 6.63 (m, 4H), 4.85 (s, 2H), 4.67 (d, 2H, J = 12.7 Hz), 4.38 (d, 2H, J = 12.4 Hz), 4.18 (q, 2H, J = 7.1 Hz), 3.87−3.71 (m, 6H), 3.16 (d, 2H, J = 13.0 Hz), 3.12 (d, 2H, J = 12.6 Hz), 2.10 (m, 2H), 1.93 (m, 4H), 1.37−1.18 (m, 45H), 1.18 (s, 9H), 1.17 (s, 9H), 0.97 (s, 18H), 0.90−0.86 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 170.90, 154.21, 153.52, 153.43, 144.88, 144.61, 144.21, 134.77, 134.27, 133.21, 133.04, 125.52, 125.14, 124.79, 124.76, 75.62, 75.38, 70.60, 60.13, 33.82, 33.80, 33.60, 31.91, 31.88, 31.53, 31.48, 31.42, 31.23, 30.88, 30.41, 30.29, 30.07, 29.94, 29.85, 29.81, 29.73, 29.69, 29.39, 29.33, 26.28, 26.19, 22.61, 14.13, 14.00; IR (thin film) 2956, 2924, 2854, 1766, 1481, 1467, 1361, 1200, 1072, 870 cm^{-1}; HRMS (FAB; M + Cs^+) calcd for $C_{78}H_{122}O_6$Cs 1287.8296, found 1287.8359.

5,11,17,23-Tetranitro-25,26,27-tris(decyloxy)-28-[(ethoxycarbonyl)methoxy]calix[4]arene (9). The calixarene **8** (7.95 g, 6.88 mmol) was dissolved in CH_2Cl_2 (100 mL) and glacial acetic acid (100 mL). To this colorless solution was added fuming HNO_3 (30 mL), resulting in a color change to an opaque purple/black. After 2 h, the clear yellow/orange solution was treated with water (250 mL) and stirred for 10 min. The organic layer was separated off, washed with water (300 mL), dried over $MgSO_4$, and filtered. Evaporation of the filtrate to dryness gave a yellow oil which upon trituration with MeOH yielded 5.83 g (5.52 mmol, 76%) of the desired product as a pale yellow powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 4H), 7.34 (m, 4H), 4.75 (s, 2H), 4.75 (d, 2H, J = 14.2 Hz), 4.51 (d, 2H, J = 13.9 Hz), 4.22 (q, 2H, J = 7.2 Hz), 4.02−3.88 (m, 6H), 3.45 (d, 2H, J = 15.2 Hz), 3.40 (d, 2H, J = 15.4 Hz), 1.89−1.85 (m, 6H), 1.56−1.27 (m, 45H), 0.90−0.86 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 168.68, 162.37, 161.34, 161.01, 143.36, 143.00, 136.08, 135.92, 134.94, 134.83, 124.61, 124.46, 123.74, 123.73, 76.47, 76.43, 70.53, 61.17, 31.79, 31.30, 30.94, 30.13, 30.02, 29.72, 29.64, 29.60, 29.55, 29.26, 29.24, 26.00, 25.71, 22.55, 14.05, 13.95; IR (thin film) 2926, 2854, 1770, 1585, 1522, 1462, 1347, 1188, 1096, 900, 745 cm^{-1}; HRMS (FAB; M + Cs^+) calcd for $C_{62}H_{86}N_4O_{14}$Cs 1243.5195, found 1243.5261.

5,11,17,23-Tetraamino-25,26,27-tris(decyloxy)-28-[(ethoxycarbonyl)methoxy]calix[4]arene (10). To the tetranitro compound **9** (0.15 g, 0.13 mmol) in toluene (20 mL) was added Raney nickel (cat.) under H_2 (atm). The mixture was heated to 50 °C for 1.5 h prior to filtration through a Celite pad. Concentration of the filtrate to dryness yielded the reduction product as a brown solid which was used without further purification (0.0903 g, 69%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.26 (s, 2H), 6.24 (s, 2H), 5.87 (s, 4H), 4.64 (s, 2H), 4.52 (d, 2H, J = 13.4 Hz), 4.30 (d, 2H, J = 13.1 Hz), 4.16 (q, 2H, J = 7.1 Hz), 3.82−3.64 (m, 6H), 3.18 (s, 8H), 2.97 (d, 4H, J = 13.7 Hz), 2.91 (d, 4H, J = 13.3 Hz), 1.83−1.79 (m, 6H), 1.42−1.24 (m, 45H), 0.90−0.86 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 170.70, 150.53, 149.49, 149.34, 140.86, 140.67, 140.42, 136.54, 136.26, 134.72, 134.64, 115.88, 115.73, 115.52, 75.26, 75.17, 70.14, 59.92, 31.79, 31.77, 31.32, 30.90, 30.07, 30.03, 29.84, 29.76, 29.71, 29.69, 29.58, 29.26, 29.22, 26.26, 25.99, 22.51, 14.04, 13.90; IR (thin film) 3350, 2924, 2853, 1765, 1608, 1468, 1379, 1216, 1184, 1078, 853 cm^{-1}; HRMS (FAB; M + Cs^+) calcd for $C_{62}H_{94}N_4O_6$Cs 1123.6228, found 1123.6279.

5,11,17,23-Tetrakis(tosylurea)-25,26,27-tris(decyloxy)-28-[(ethoxycarbonyl)methoxy]calix[4]arene (11). The tetraamino compound **10** (0.090 g, 0.091 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under N_2. To the homogeneous solution was added *p*-toluenesulfonyl isocyanate (70 μL, 0.46 mmol), and the reaction was stirred at room temperature for 4 h. The solvent was then removed in vacuo, and the resulting solid was triturated with MeOH. This process was repeated, and the resulting suspension was filtered. The urea (0.145 g, 90%) was used without further purification: H NMR (600 MHz, DMF-d_7) δ 10.39 (bs, 2H), 10.26 (bs, 2H), 8.67 (s, 1H), 8.66 (s, 1H), 8.44 (s, 2H), 7.97 (d, 4H, J = 8.2 Hz), 7.93 (d, 4H, J = 8.3 Hz), 7.49 (d, 4H, J = 8.2 Hz), 7.46 (d, 4H, J = 8.2 Hz), 6.89 (s, 2H), 6.88 (s, 2H), 6.54 (s,

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4H), 4.74 (s, 2H), 4.58 (d, 2H, J = 13.3 Hz), 4.34 (d, 2H, J = 13.0 Hz), 3.84 (m, 2H), 3.81−3.72 (m, 4H), 3.08 (d, 2H, J = 14.0 Hz), 3.06 (d, 2H, J = 13.6 Hz), 2.45 (s, 6H), 2.44 (s, 6H), 1.92−1.84 (m, 6H), 1.46−1.24 (m, 44H), 1.25 (t, 3H, J = 7.2 Hz), 0.91−0.86 (m, 9H); ^{13}C NMR (DMF-d_7) δ 170.88, 153.87, 153.41, 152.99, 150.48, 145.23, 145.17, 138.77, 138.73, 136.44, 136.29, 135.40, 135.32, 133.82, 133.52, 133.20, 130.54, 130.50, 128.88, 128.84, 120.48, 120.45, 120.29, 120.24, 76.20, 71.42, 60.97, 32.67, 32.65, 32.03, 31.54, 30.97, 30.91, 30.76, 30.65, 30.60, 30.51, 30.49, 30.13, 27.17, 26.99, 23.33, 21.52, 14.66, 14.46; IR (thin film) 3350, 2924, 2854, 1762, 1694, 1599, 1550, 1464, 1343, 1218, 1162, 1091, 895, 667 cm^{-1}; LRMS (ESI; M + Na$^+$ + ^{13}C) calcd for $C_{94}H_{122}N_8O_{18}S_4Na$ 1752, found 1752.

5,11,17,23-Tetrakis(tosylurea)-25,26,27-tris(decyloxy)-28-(carboxymethoxy)calix[4]arene (12). The ester **11** (0.139 g, 0.0778 mmol) was dissolved in a mixture of THF (7.5 mL) and water (1.5 mL). To this suspension was added LiOH·H_2O (0.065 g, 1.6 mmol), and the mixture was stirred at room temperature for 18 h. After this period, the resulting solution was poured into 50 mL of water and treated with 1 M HCl until strongly acidic. The tan precipitate was filtered and washed with water, yielding 0.123 g (0.0702 mmol, 90%) of the crude acid: ^{1}H NMR (600 MHz, DMF-d_7) δ 12.65 (bs, 1H), 10.38 (bs, 2H), 10.30 (bs, 2H), 8.64 (s, 1H), 8.61 (s, 1H), 8.53 (s, 2H), 7.96 (d, 4H, J = 8.3 Hz), 7.94 (d, 4H, J = 8.3 Hz), 7.48 (d, 4H, J = 7.8 Hz), 7.47 (d, 4H, J = 7.8 Hz), 6.80 (s, 4H), 6.68 (s, 4H), 4.63 (s, 2H), 4.54 (d, 2H, J = 13.2 Hz), 4.36 (d, 2H, J = 12.9 Hz), 3.89−3.77 (m, 6H), 3.09 (d, 2H, J = 13.2 Hz), 3.07 (d, 2H, J = 12.9 Hz), 2.45 (s, 6H), 2.45 (s, 6H), 1.91−1.85 (m, 6H), 1.41−1.23 (m, 43H), 0.88−0.86 (m, 9H); ^{13}C NMR (DMF-d_7) δ 171.37, 153.08, 152.81, 152.24, 149.98, 149.95, 144.64, 138.21, 135.58, 135.40, 135.23, 135.11, 133.30, 132.93, 132.80, 129.97, 128.30, 128.29, 119.91, 119.87, 119.79, 75.80, 71.13, 32.14, 32.12, 31.44, 31.00, 30.34, 30.21, 30.15, 30.10, 30.06, 30.03, 29.94, 29.61, 26.50, 26.45, 22.79, 20.97, 13.93; IR (thin film) 3350, 2925, 2854, 1706, 1599, 1552, 1466, 1341, 1218, 1163, 1090, 1055, 894, 664 cm^{-1}; LRMS (ESI; M + H$^+$) calcd for $C_{92}H_{119}N_8O_{18}S_4$ 1752, found 1752.

1,8-Bis{5,11,17,23-tetrakis(tosylurea)-25,26,27-tris(decyloxy)-28-[(aminocarbonyl)methoxy]calix[4]arene}octane (3b). The above acid **12** (0.0742 g, 0.0423 mmol) was dissolved in anhydrous DMF (3 mL) under N_2. To this solution was added PyBOP[14] (0.033 g, 0.064 mmol), triethylamine (35 μL, 0.254 mmol), and 1,8-diaminooctane (0.0029 g, 0.020 mmol). The reaction solution was stirred for 14 h at 35 °C. Most of the DMF was removed in vacuo, and the resulting yellow oil was diluted to 20 mL with $CHCl_3$. This solution was washed with 1 M HCl (2 × 30 mL) and brine (2 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to dryness. Trituration with MeOH gave the product as a beige powder (0.0495 g, 68%): ^{1}H NMR (600 MHz, DMF-d_7) δ 10.33 (bs, 8H), 8.59 (s, 4H), 8.58 (s, 2H), 8.54 (s, 2H), 7.96 (d, 8H, J = 8.1 Hz), 7.94 (d, 8H, J = 8.3 Hz), 7.48−7.44 (m, 16H), 6.74 (s, 8H), 6.68 (s, 4H), 6.67 (s, 4H), 4.41 (d, 4H, J = 13.3 Hz), 4.37 (s, 4H), 4.33 (d, 4H, J = 12.9 Hz), 3.96−3.92 (m, 4H), 3.88−3.84 (m, 4H), 3.76 (m, 4H), 3.31−3.29 (m, 4H), 3.11 (d, 4H, J = 13.5 Hz), 3.07 (d, 4H, J = 13.3 Hz), 2.44 (s, 12H), 2.44 (s, 12H), 1.91−1.82 (m, 16H), 1.50 (m, 8H), 1.35−1.30 (m, 82H), 0.88−0.86 (m, 18H); IR (thin film) 3342, 2924, 2853, 1686, 1608, 1555, 1458, 1340, 1225, 1090, 1055, 892 cm^{-1}.

Ethyl 4-{2-{3,5-Bis{2-[4-(ethoxycarbonyl)phenyl]-1-ethynyl}-phenyl}-1-ethynyl}benzoate (14).[16] To a solution of ethyl 4-iodobenzoate (0.89 mL, 5.3 mmol) in diethylamine (25 mL) was added $Pd(PPh_3)_2Cl_2$ (0.047 g, 0.067 mmol) and CuI (0.038 g, 0.20 mmol) under N_2. The resulting green mixture was treated with triethynylbenzene[15] (0.195 g, 1.33 mmol) and stirred at room temperature. After 30 min, the solution assumed a bright yellow color which gradually changed to orange over the course of several hours.

After 20 h, the reaction was deemed near completion by TLC (5:1 hexanes/EtOAc; desired product R_f = 0.4). The DEA was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (70 mL) and washed with water (100 mL). The aqueous layer was back-extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic layers were dried over $MgSO_4$ and filtered. To the filtrate was added 10 mL of SiO_2 and the solvent was removed. The preload was added to a 150-mL SiO_2 column and eluted with 6:1 hexanes/EtOAc. Evaporation of the desired fractions gave the product as a pale yellow powder (0.181 g, 23%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 6H, J = 6.7 Hz), 7.71 (s, 3H), 7.59 (d, 6H, J = 6.8 Hz), 4.40 (q, 6H, J = 7.2 Hz), 1.41 (t, 9H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 166.11, 134.66, 131.66, 130.35, 129.64, 127.22, 123.82, 90.23, 90.05, 61.17, 14.18; IR (thin film) 2983, 2890, 2247, 1715, 1695, 1604, 1404, 1366, 1307, 1276, 1175, 1128, 1107, 1019, 918, 768, 732 cm^{-1}; HRMS (FAB; M + H$^+$) calcd for $C_{39}H_{31}O_6$ 595.2121, found 595.2140.

4-{2-{3,5-Bis[2-(4-carboxyphenyl)-1-ethynyl]phenyl}-1-ethynyl}-benzoic acid (15). The ester **14** (0.150 g, 0.252 mmol) was dissolved in a mixture of THF (4 mL) and H_2O (0.6 mL). To this was added LiOH·H_2O (0.212 g, 5.04 mmol), and the mixture was stirred at room temperature. H_2O (2 mL) was added over the course of several hours as the ester reacted and solubility increased. After 14 h, the reaction was determined complete by TLC (EtOAc). The solution was poured into 40 mL of H_2O and acidified with 1 M HCl. Evaporation of all solvents gave the crude product (0.138 g, quantitative) as a tan powder. Trituration with MeOH gave the pure triacid as a white powder (0.063 g, 49%): ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.22 (bs, 3H), 8.00 (d, 6H, J = 8.3 Hz), 7.88 (s, 3H), 7.72 (d, 6H, J = 8.3 Hz): ^{13}C NMR (DMSO-d_6) δ 166.91, 134.67, 131.95, 131.19, 129.81, 126.14, 123.54, 90.34, 89.88; IR (thin film) 3007 (b), 2209, 1723, 1693, 1605, 1581, 1558, 1417, 1312, 1280, 1176, 1108, 1017, 877, 857, 770 cm^{-1}. LRMS (ESI; M − H) calcd for $C_{33}H_{18}O_6$ 509, found 509.

BOC-Protected Calixarene (17). The acid **16**[4] (0.543 g, 0.353 mmol) was dissolved in anhydrous DMF (10 mL) under N_2. To this solution was added PyBOP (0.221 g, 0.424 mmol), triethylamine (59 μL, 0.42 mmol), and mono-BOC-protected p-xylylenediamine[17] (0.10 g, 0.424 mmol). After the mixture was stirred at room temperature for 1 h, most of the DMF was removed in vacuo and the resulting brown oil was diluted with CH_2Cl_2 (50 mL). This solution was washed with 1 M NaOH (2 × 50 mL) and brine (2 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to near dryness. Trituration with MeOH gave the product as an off-white powder (0.504 g, 81%): ^{1}H NMR (600 MHz, DMF-d_7) δ 8.80 (t, 1H, J = 6.0 Hz), 8.60 (bs, 2H), 8.58 (s, 1H), 8.55 (s, 1H), 8.34 (s, 2H), 8.30 (s, 2H), 7.44 (d, 2H, J = 8.5), 7.43 (d, 2H, J = 8.5), 7.38 (d, 2H, J = 8.0 Hz), 7.34 (d, 2H, J = 8.1 Hz), 7.28 (t, 1H, J = 6.0 Hz), 7.26 (d, 4H, J = 8.5 Hz), 7.20 (s, 2H), 7.18 (s, 2H), 7.13 (d, 2H, J = 8.5 Hz), 7.12 (d, 2H, J = 8.6 Hz), 7.05 (d, 4H, J = 8.5 Hz), 6.63 (bs, 4H), 4.79 (s, 2H), 4.69 (d, 2H, J = 5.9 Hz), 4.51 (d, 2H, J = 13.5 Hz), 4.43 (d, 2H, J = 13.2 Hz), 4.26 (d, 2H, J = 6.2 Hz), 3.90 (m, 2H), 3.80−3.74 (m, 4H), 3.24 (d, 2H, J = 13.8 Hz), 3.18 (d, 2H, J = 13.5 Hz), 2.56−2.51 (m, 8H), 1.87 (m, 2H), 1.74 (m, 4H), 1.57 (m, 8H), 1.41 (s, 9H), 1.32−1.24 (m, 32H), 0.93 (t, 3H, J = 7.4 Hz), 0.90 (t, 6H, J = 7.4 Hz), 0.88−0.85 (m, 12H); ^{13}C NMR (DMF-d_7) δ 170.42, 156.71, 153.55, 153.51, 153.39, 153.12, 152.25, 150.95, 139.80, 138.74, 138.66, 138.61, 138.59, 136.44, 136.38, 136.33, 135.96, 135.09, 134.98, 134.86, 134.59, 133.83, 129.01, 128.86, 127.81, 127.38, 119.64, 119.45, 119.23, 119.06, 118.69, 118.67, 118.32, 78.16, 77.56, 76.62, 74.74, 43.89, 42.23, 35.13, 32.03, 31.93, 31.59, 29.33, 29.27, 28.17, 23.11, 22.93, 22.74; IR (thin film) 3339, 3189, 3119, 2957, 2926, 2854, 1718, 1667, 1605, 1552, 1514, 1476, 1418, 1316, 1214, 1052, 1002, 848 cm^{-1}; HRMS (FAB; M + Cs$^+$) calcd for $C_{108}H_{142}N_{10}O_{11}Cs$ 1887.9914, found 1887.9993.

BOC Deprotection (18). To a solution of the protected amine **17** (0.30 g, 0.17 mmol) in dioxane (30 mL) was bubbled HCl(g). After 20 min, the precipitation of a solid was observed and the deprotection was determined complete after 50 min by TLC (20:1 CH_2Cl_2/MeOH). The solvent was removed in vacuo, giving the crude amine salt which was used without further purification (0.288 g, 99%): HRMS (FAB; M + Cs$^+$ − HCl) calcd for $C_{103}H_{134}N_{10}O_9Cs$ 1787.9390, found 1787.9497.

Coupling of 18 to the C_3-Symmetric Spacer (19). To a solution of the triacid **15** (0.027 g, 0.053 mmol) and PyBOP (0.088 g, 0.17 mmol) in DMF (5 mL) was added a solution of the amine **18** (0.288 g, 0.170 mmol) and NEt_3 (89 uL, 0.64 mmol) in DMF (5 mL). The homogeneous solution was stirred at room temperature for 5 h, when the reaction was determined complete by TLC (20:1 CH_2Cl_2/MeOH). The DMF was removed in vacuo, and the residue was dissolved in CH_2Cl_2. Washing with 1 M HCl (2 × 30 mL) yielded an emulsion.

Additional washing with 1 M NaOH and brine did not yield a clean separation. The combined aqueous extracts containing the emulsion were treated with THF, and the resulting clear, biphasic mixture was separated off. All of the organic layers were combined (THF + CH_2Cl_2), dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the crude solid was chromatographed on SiO_2 (160 mL, 20:1 CH_2Cl_2/MeOH, $R_f = 0.50$). Fractions containing the lower R_f of two product spots were combined and concentrated, giving the desired product as a pale yellow powder (0.271 g, 94%). ^{1}H NMR (600 MHz, DMF-d_7) δ 9.15 (t, 3H, $J = 6.0$ Hz), 8.81 (t, 3H, $J = 6.2$ Hz), 8.61 (s, 3H), 8.58 (s, 3H), 8.55 (s, 3H), 8.53 (s, 3H), 8.30 (s, 6H), 8.29 (s, 6H), 8.10 (d, 6H, $J = 8.3$ Hz), 7.86 (s, 3H), 7.77 (d, 6H, $J = 8.3$ Hz), 7.47−7.36 (m, 24H), 7.26 (d, 12H, $J = 8.4$), 7.18 (d, 12H, $J = 8.0$), 7.11 (d, 12H, $J = 8.3$ Hz), 7.06 (d, 12H, $J = 8.4$ Hz), 6.64 (s, 6H), 6.64 (s, 6H), 4.79 (s, 6H), 4.69 (d, 6H, $J = 5.6$ Hz), 4.63 (d, 6H, $J = 4.8$ Hz), 4.51 (d, 6H, $J = 13.6$ Hz), 4.43 (d, 6H, $J = 13.1$ Hz), 3.90 (m, 6H), 3.80−3.75 (m, 12H), 3.24 (d, 6H, $J = 13.8$ Hz), 3.18 (d, 6H, $J = 13.8$ Hz), 2.56−2.51 (m, 24H), 1.88 (m, 6H), 1.74 (m, 12H), 1.57 (m, 24H), 1.30−1.25 (m, 96H), 0.93 (t, 9H, $J = 7.4$ Hz), 0.90 (t, 18H, $J = 7.4$ Hz), 0.88−0.85 (m, 36H). IR (KBr) 3326, 2926, 2855, 2208, 1667, 1600, 1548, 1469, 1416, 1311, 1210, 1014 cm^{-1}. LRMS (MALDI; M_{avg}) calcd for $C_{342}H_{414}N_{30}O_{30}$ 5425, found 5427.

5,11,17,23-Tetrakis(tosylurea)-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (21). Prepared similarly to **11** using 0.288 g (0.413 mmol) of the tetraamine[4] and 316 μL (2.07 mmol) of *p*-toluenesulfonyl isocyanate. The product was obtained as an off-white powder and used without further purification (0.343 g, 56%): ^{1}H NMR (600 MHz, DMF-d_7) δ 10.46 (bs, 2H), 10.19 (bs, 2H), 8.72 (s, 1H), 8.71 (s, 1H), 8.41 (s, 2H), 7.98 (d, 4H, $J = 8.2$ Hz), 7.92 (d, 4H, $J = 8.4$ Hz), 7.50 (d, 4H, $J = 8.3$ Hz), 7.46 (d, 4H, $J = 8.3$ Hz), 6.94 (s, 2H), 6.93 (s, 2H), 6.47 (s, 4H), 4.74 (s, 2H), 4.58 (d, 2H, $J = 13.3$ Hz), 4.33 (d, 2H, $J = 13.0$ Hz), 4.15 (q, 2H, $J = 7.0$ Hz), 3.83−3.66 (m, 6H), 3.08 (d, 2H, $J = 13.2$ Hz), 3.06 (d, 2H, $J = 13.0$ Hz), 2.46 (s, 6H), 2.44 (s, 6H), 1.92−1.82 (m, 6H), 1.23 (t, 3H, $J = 7.2$ Hz), 0.98 (t, 6H, $J = 7.4$ Hz), 0.93 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (DMF-d_7) δ 170.50, 153.41, 152.76, 152.68, 149.96, 149.95, 144.71, 144.63, 138.22, 138.16, 136.07, 135.89, 134.66, 134.58, 133.27, 133.00, 132.58, 130.00, 129.95, 128.34, 128.29, 119.96, 119.72, 119.69, 77.24, 77.09, 70.99, 60.44, 31.45, 30.99, 23.23, 20.98, 20.97, 14.03, 10.34, 9.90; IR (KBr) 3353, 3242 (b), 2963, 2925, 2872, 1718, 1599, 1544, 1458, 1343, 1218, 1162, 892 cm^{-1}; LRMS (ESI; M + Na$^+$) calcd for $C_{73}H_{80}N_8O_{18}Na$ 1508, found 1508.

5,11,17,23-Tetrakis(tosylurea)-25,26,27-tripropoxy-28-(carboxymethoxy)calix[4]arene (22). Prepared similarly to **12** using 0.100 g (0.0672 mmol) of **21** and 0.056 g (1.35 mmol) of LiOH·H_2O. The white solid obtained was used without further purification (0.086 g, 88%): ^{1}H NMR (600 MHz, DMF-d_7) δ 12.49 (bs, 1H), 10.49 (bs, 2H), 10.24 (bs, 2H), 8.75 (s, 1H), 8.73 (s, 1H), 8.46 (s, 2H), 7.98 (d, 4H, $J = 8.3$ Hz), 7.93 (d, 4H, $J = 8.2$ Hz), 7.49 (d, 4H, $J = 8.2$ Hz), 7.46 (d, 4H, $J = 8.3$ Hz), 6.94 (s, 2H), 6.94 (s, 2H), 6.55 (s, 2H), 6.55 (s, 2H), 4.67 (s, 2H), 4.54 (d, 2H, $J = 13.2$ Hz), 4.36 (d, 2H, $J = 12.9$ Hz), 3.85 (m, 2H), 3.77−3.68 (m, 4H), 3.10 (d, 2H, $J = 12.4$ Hz), 3.08 (d, 2H, $J = 12.4$ Hz), 2.45 (s, 6H), 2.44 (s, 6H), 1.90−1.82 (m, 6H), 0.96 (t, 6H, $J = 7.5$ Hz), 0.91 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (DMF-d_7) δ 171.52, 153.28, 152.51, 152.44, 150.00, 149.96, 144.74, 144.67, 138.25, 138.20, 136.05, 135.81, 134.83, 134.66, 133.48, 133.09, 132.75, 130.03, 129.99, 128.35, 128.30, 120.06, 119.90, 119.84, 77.50, 77.27, 71.01, 31.43, 31.01, 23.18, 20.98, 21.00, 10.26, 9.89; IR (thin film) 3353, 3189, 2966, 2876, 1709, 1599, 1552, 1466, 1342, 1218, 1162, 1054, 890, 663 cm^{-1}; LRMS (ESI; M − H) calcd for $C_{71}H_{75}N_8O_{18}$ 1455, found 1455.

1-{[5,11,17,23-tetrakis(*p*-heptylphenyl)-25,26,27-tripropoxy-28-[(aminocarbonyl)methoxy]calix[4]arene]-4-[5,11,17,23-tetrakis-(tosylurea)-25,26,27-tripropoxy-28-[(aminocarbonyl)methoxy]calix-[4]arene]}xylene (3c). The tripropoxy sulfonyl acid **22** (0.0537 g, 0.0368 mmol) was dissolved in anhydrous DMF (4 mL) under N_2. To this solution was added PyBOP (0.023 g, 0.044 mmol), and the solution was stirred at room temperature for several minutes. In a separate flask, the amine hydrochloride **18** (0.0623 g, 0.0368 mmol) was treated with triethylamine (20 μL, 0.15 mmol), and this solution was transferred to the flask containing the acid. The reaction was continued at room temperature for 2.5 h. Most of the DMF was removed in vacuo, and the resulting oil was diluted to 20 mL with $CHCl_3$. This solution was washed with 1 M HCl (2 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness. Trituration with MeOH gave the crude product as an off-white powder (0.0791 g, 69%): ^{1}H NMR (600 MHz, DMF-d_7) δ 10.47 (s, 1H), 10.43 (s, 1H), 10.20 (s, 2H), 8.81 (t, 1H, $J = 5.7$ Hz), 8.72 (s, 1H), 8.68 (s, 1H), 8.60 (t, 1H, $J = 6.1$ Hz), 8.56 (s, 1H), 8.55 (s, 1H), 8.53 (s, 1H), 8.52 (s, 1H), 8.43 (s, 2H), 8.27 (s, 4H), 7.96 (s, 2H), 7.95 (s, 2H), 7.90 (d, 4H, $J = 8.3$ Hz), 7.47 (d, 2H, $J = 8.2$ Hz), 7.46 (d, 2H, $J = 8.3$ Hz), 7.43 (d, 4H, $J = 8.0$ Hz), 7.37 (d, 2H, $J = 8.2$ Hz), 7.34 (d, 2H, $J = 8.2$ Hz), 7.25 (d, 4H, $J = 8.4$ Hz), 7.18 (s, 2H), 7.18 (s, 2H), 7.12 (d, 4H, $J = 8.5$ Hz), 7.05 (d, 4H, $J = 8.5$ Hz), 6.88 (s, 2H), 6.88 (s, 2H), 6.62 (s, 4H), 6.47 (s, 2H), 6.46 (s, 2H), 4.78 (s, 2H), 4.67 (d, 2H, $J = 5.9$ Hz), 4.62 (s, 2H), 4.58 (d, 2H, $J = 5.8$ Hz), 4.46 (d, 2H, $J = 11.2$ Hz), 4.42 (d, 2H, $J = 13.4$ Hz), 4.40 (d, 2H, $J = 12.9$ Hz), 4.29 (d, 2H, $J = 13.1$ Hz), 3.87 (m, 2H), 3.79−3.70 (m, 10H), 3.21 (d, 2H, $J = 13.8$ Hz), 3.16 (d, 2H, $J = 13.4$ Hz), 3.08 (d, 2H, $J = 13.8$ Hz), 3.05 (d, 2H, $J = 13.5$ Hz), 2.52 (m, 8H), 2.43 (s, 3H), 2.43 (s, 3H), 2.41 (s, 6H), 1.78−1.66 (m, 12H), 1.56−1.53 (m, 8H), 1.29−1.24 (m, 32H), 0.92−0.79 (m, 30H); IR (thin film) 3358, 2926, 2854, 1715, 1670, 1602, 1554, 1511, 1476, 1215, 1150 cm^{-1}.

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Supporting Information Available: Additional GPC data and NOESY/ROESY data for **2** (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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