Orthogonal, Convergent Syntheses of Dendrimers Based on Melamine with One or Two Unique Surface Sites for Manipulation

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Abstract: An orthogonal, convergent route for the introduction of substoichiometric numbers of latent surface sites into dendrimers based on melamine is used to prepare targets that display one or two Boc-protected amines on the periphery. Asymmetry is the result of the stepwise incorporation of functionalized and unfunctionalized dendrons onto the triazine cores, a highly selective process due to the different reactivities of the substituted triazines. The routes to the dendrons rely on iterative reactions of the growing dendrons with triazine cores and diamine linkers. *p*-Aminobenzylamine is used as a linking group to avoid functional group interconversions or protecting group manipulations. Addition of the benzylamine group to the monochlorotriazine of the dendron proceeds cleanly leaving a less reactive aniline for subsequent reaction with trichlorotriazine. The routes to these targets proceed in 5 or 6 linear steps (11 or 12 total steps) in 40% overall yield. The unique surface sites can be deprotected and subjected to additional chemistries. Reaction of the monofunctionalized dendrimer with trichlorotriazine yields the desired dimer, a molecule whose increased size is evident from light scattering and tapping mode atomic force microscopy, and corroborated with computation.

Introduction

The belief that structural diversity will lead ultimately to functional utility inspires the synthetic dendrimer community.[1−3] Thus, the synthesis of dendrimers that display specific patterns of groups that are amenable to postsynthetic manipulation is an area of great interest. The complexity of these targets varies significantly in both the number and arrangement of groups. Typically the result of divergent syntheses, dendrimers terminated with latent or reactive surface groups are common, but these molecules cannot be manipulated to generate single or well-defined patterns of multiple functional groups.[4−7] Of the many examples of amine- and hydroxy-terminated dendrimers, three are commercially available: poly(amidoamine) from Dendritech (Midland, MI), poly(propyleneimine) from DSM (Netherlands), and hyperbranched polyester polyols from Perstorp (Sweden). Engineering fewer sites for manipulation greatly increases the synthetic challenge.

The first example of a dendrimer displaying a single latent group for postsynthetic manipulation was reported from Fréchet's laboratory. Hawker[8] and Wooley[9] employed convergent approaches to prepare a dendrimer incorporating a single nitrile that could be reduced to afford an amine. While neither orthogonal nor trivial in execution, it remained the solitary example of a monofunctionalized dendrimer for almost 10 years. Recently, Schluter and co-workers reported dendrimers synthesized using Hawkers's original strategy that display a single aromatic bromide at three different positions including one near the surface. Schluter has shown that the arylbromide can be cross-coupled with 4-*tert*-butylphenylboronic acids under Suzuki conditions to incorporate groups at specific positions within the dendrimer.[10] Here, we describe the synthesis and characterization of a new class of dendrimers based on melamine with one or two protected amine sites on the surface. The syntheses of targets **1** and **2** are orthogonal and convergent, can be executed expeditiously, and proceed in excellent overall yields.

Our long-term goal is to develop routes that afford specific control over the placement of diversity both on the interior and periphery of dendrimers. Dendrimers based on melamine offer an opportunity to generate diversity in a synthetically tractable manner.[11] While the syntheses of Hawker, Wooley, and Schluter using Fréchet-type dendrimers have successfully exploited statistical reactions biased by sterics to obtain asymmetry, we use the differential reactivity of the triazines. By controlling the temperature, *N*,*N*′,*N*″-trisubstituted triazines can be obtained by sequential addition of amines (Scheme 1). Yields exceeding 90% are routine for these one-pot reactions. Employing diamines offers an opportunity to interconnect triazines to afford dendrimers.

Here, we use *p*-aminobenzylamine to interconnect triazines to avoid functional group interconversions and protecting group manipulations. The benzylic amine reacts exclusively with monochlorotriazines leaving a less reactive arylamine for

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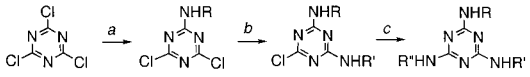
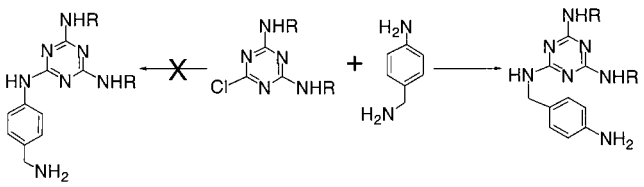
Scheme 1. Differential Reactivity of Triazines



[a] RNH_2 at 0 °C in THF with diisoproylethylamine (DIPEA). [b] $R'NH_2$ at 25 °C in THF with DIPEA. [c] $R''NH_2$ at 80 °C in THF with DIPEA.

Scheme 2. Chemoselective Reaction Affords an Orthogonal Route to These Dendrimers



reaction with the subsequent trichlorotriazine core (Scheme 2). This orthogonal strategy differs from routes described by Zimmerman,[12] Yu,[13] Fréchet,[14] and Kakimoto[15] in that chemoselectivity and not orthogonal reactivity is used.

Results and Discussion

The convergent route to the preparation of dendrimers with a unique surface site(s) requires reaction of trichlorotriazine with the functionalized and unfunctionalized dendrons at each generation. The dendron syntheses are described individually beginning with the unfunctionalized dendrons, molecules that serve as reagents in our discussion of the synthesis of functionalized dendrons.

Synthesis of Unfunctionalized Dendrons. Scheme 3 shows the synthesis of the unfunctionalized dendrons used to construct **1** and **2**. The route entails iterative reactions of cyanuric chloride and *p*-aminobenzylamine. Butyl groups on the periphery are large enough to convey solubility in organic solvents, while being small enough to afford crystalline (as opposed to waxlike) solids.

Monochlorotriazine **3** is available in one step from butylamine and trichlorotriazine. Reaction with *p*-aminobenzylamine at elevated temperatures proceeds specifically to provide the desired aniline, **4**, in excellent yield. Reaction with 0.5 equiv of trichlorotriazine in the presence of Hunig's base at low temperature provides **5**, which is elaborated with *p*-aminobenzylamine to **6**. Reaction of **6** with trichlorotriazine yields **7**. Piperazine is more reactive than primary amines, and is suited ideally for reaction with another hindered monochlorotriazine dendron. The reaction of **7** to yield **8** proceeds cleanly using excess piperazine. All molecules are soluble in a range of organic solvents, allowing purification by conventional silica gel chromatography to give satisfactory ^1H and ^{13}C NMR and mass spectra.

Throughout our iterative approach to these dendrimers, we choose to isolate the monochlorotriazine instead of elaborating to the amine in a single, one-pot sequence. That is, starting with **4**, we *could* proceed to **6** without isolating or purifying intermediate **5** by addition of the *p*-aminobenzylamine linker in one pot. Our primary motivation for using a multipot protocol is purification and characterization. The differences in polarity between the anilines and monochlorotriazines is significant, allowing us to monitor the stepwise displacement of chlorine atoms from triazines by TLC, and offering easy separation of these materials after reaction. The difference in polarity between two anilines is not significant at higher generations.

Synthesis of the Functionalized Dendrons. Scheme 4 shows the synthesis of the functionalized dendrons. The Boc-protected diamine selected offers a long, flexible handle that we subsequently show to be available for additional chemistries, and provides characteristic lines in an uncrowded region of the ^1H NMR spectrum. Synthesis of **9** proceeds in 86% overall yield through the sequential addition of Boc-protected amine to trichlorotriazine at low temperature (0 °C) followed by addition of butylamine at room temperature. Elaboration with *p*-aminobenzylamine at elevated temperature (70 °C) proceeds selectively to yield aniline **10**. To obtain **11**, trichlorotriazine is reacted first with **4** at −10 °C. TLC reveals only the formation of the dichlorotriazine intermediate. Following the addition of **10**, the reaction is warmed to room temperature and monitored for disappearance of the dichlorotriazine and appearance of **11**. After purification by silica gel chromatography, NMR spectroscopy and mass spectrometry do not provide any evidence of **5**, a product that might result from reaction of 2 equiv of **4** with trichlorotriazine. Similarly, no evidence for the product resulting from reaction of 2 equiv of **10** with trichlorotriazine is observed. Reaction of **11** with *p*-aminobenzylamine provides aniline **12** cleanly. Careful addition of **6** to trichlorotriazine followed by addition of **12** provides **13**. Again, the entire reaction sequence to provide **13** can be monitored easily by TLC to ensure complete reaction at each stage.

Synthesis of Dendrimers. Reaction of **8** with **13** affords the monofunctionalized dendrimer **1** (Scheme 5). Reacting 2 equiv of **13** with piperazine yields **2**. Assessing the overall purity of these molecules is difficult. The ^1H NMR spectra of these molecules do not reveal impurities, but the broad lines can obscure any such observation. Mass spectrometry provides evidence for contamination: a line corresponding to the reaction product of **7** and **8** (yielding the unfunctionalized, all-butyl terminated dendrimer) is evident in the spectra of **1**. We estimate the impurity exists at <3% based on doping samples of **1** with a sample of the all-butyl dendrimer that we prepared as a control. Trace amounts of dendron **7** that contaminate dendron **12** can lead to the appearance of dendrimer **1** in preparations of dendrimer **2**. A line corresponding to **1** appears in the mass spectrum of **2** at <3% relative intensity.

Manipulation of Unique Surface Sites. Treatment of dendrimers **1** and **2** with a 1:1 solution of trifluoroacetic acid and dichloromethane provides quantitative deprotection (Scheme 6). Molecules **14** and **15** are purified using silica gel chromatography. Encouragingly, neither the NMR nor mass spectra of the resulting products show evidence of impurities. The amine groups can be acylated with isocyanates or reacted with trichlorotriazine. Indeed, reaction of **14** with 0.5 equiv of trichlorotriazine provides dimer **16**. Efforts to polymerize **15** with bisisocyanates to provide a popcorn-on-a-string motif have yielded precipitates that are the object of further study.

Characterization. In addition to ^1H and ^{13}C NMR spectroscopy, and mass spectrometry, the dendrimers were characterized by light scattering and atomic force microscopy to evaluate differences in size. Computational models corroborate experimental results. Combustion analyses proved satisfactory for dendrimer−solvent complexes. The targets did not provide traces by size exclusion chromatography.

(a) NMR Spectroscopy. Both the ^{13}C and ^1H NMR spectroscopy reveal clues of the iterative nature of the synthesis. While some of this detail is obscured by the broadening of the

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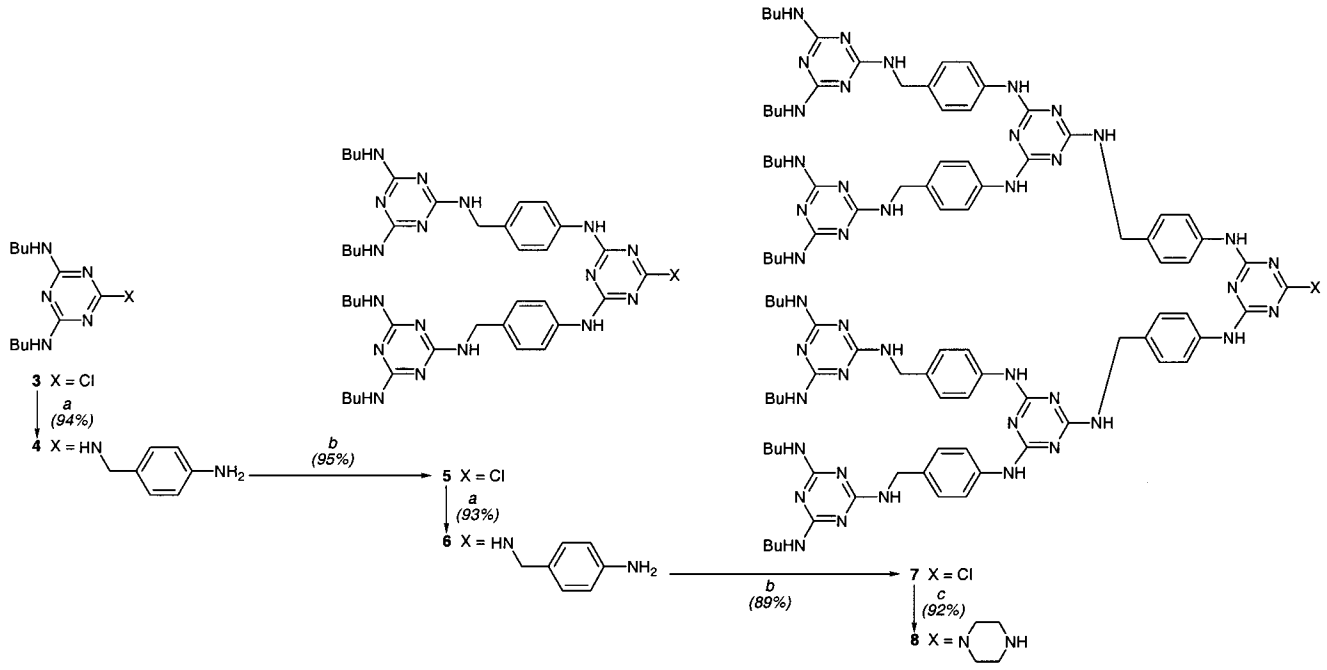
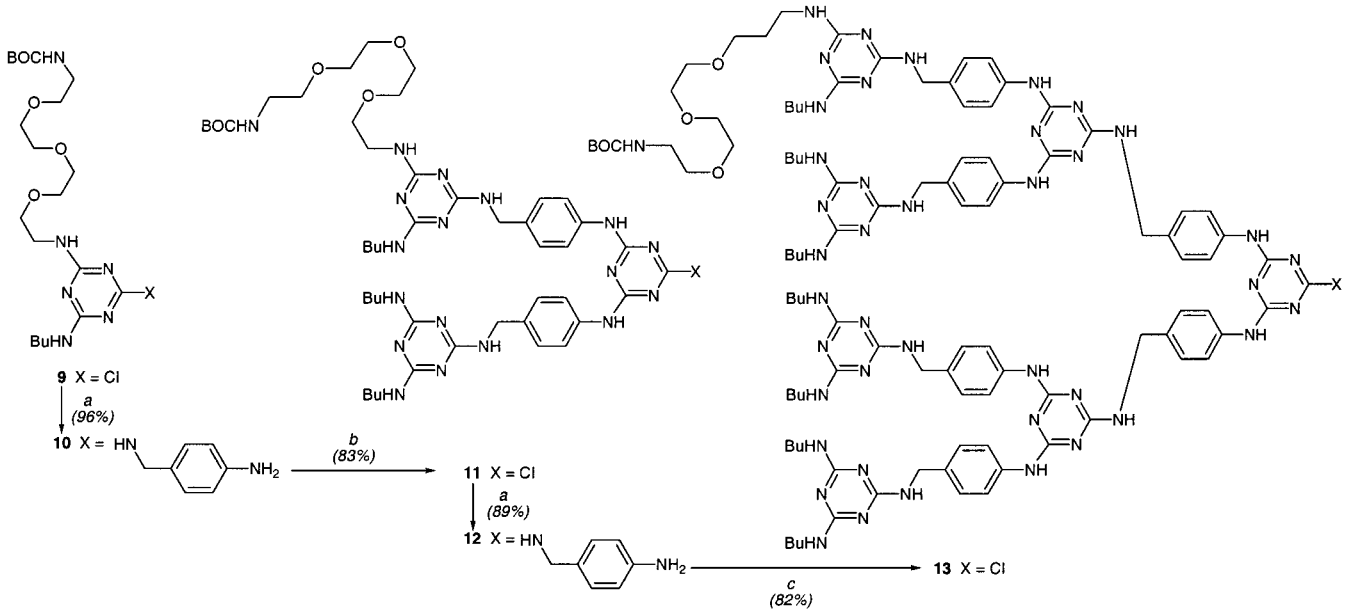
Scheme 3. Synthesis of the Unfunctionalized Dendrons



[a] *p*-Aminobenzylamine at 70 °C in THF with DIPEA. [b] $C_3N_3Cl_3$ (0.5 equiv) at 0 °C in THF with DIPEA. [c] Excess piperazine.

Scheme 4. Synthesis of the Functionalized Dendrons



[a] *p*-Aminobenzylamine at 70 °C in THF with DIPEA. [b] Room temperature; after addition of **4** at −10 °C to $C_3N_3Cl_3$ in THF with DIPEA. [c] Room temperature to 40 °C; after addition of **6** at −10 °C to $C_3N_3Cl_3$ in THF with DIPEA.

lines of the ^{1}H NMR, the appearance of the aniline resonance and positions of the benzylic and aromatic protons of the *p*-aminobenzylamine are indicative of the extent of reaction.[16] We attribute the broadness of the spectra to many factors including rotational isomers about the triazine linkage (single bond isomers arising from hindered rotation of the triazine ring−NHR bond) and intra- and intermolecular hydrogen bonding.[17−19] Indeed, the ^{1}H NMR recorded in DMSO-d_6 of larger dendrons and the dendrimers reveal hydrogen bonding: exchangeable melamine protons appear downfield at ∼9 ppm; multiple broad peaks appear between 7 and 8 ppm.[20]

Similar trends in the appearance and disappearance of lines in the ^{13}C spectra corresponding to aromatic carbons of

(16) This trend has been verified by the synthesis of larger generation dendrons based on *p*-aminobenzylamine: Zhang, W.; Simanek, E. E. *Tetrahedron Lett.* **2001**, in press.

(17) Such broadness is useful for studying self-assembling aggregates based on polymelamines. See, for example: Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37.

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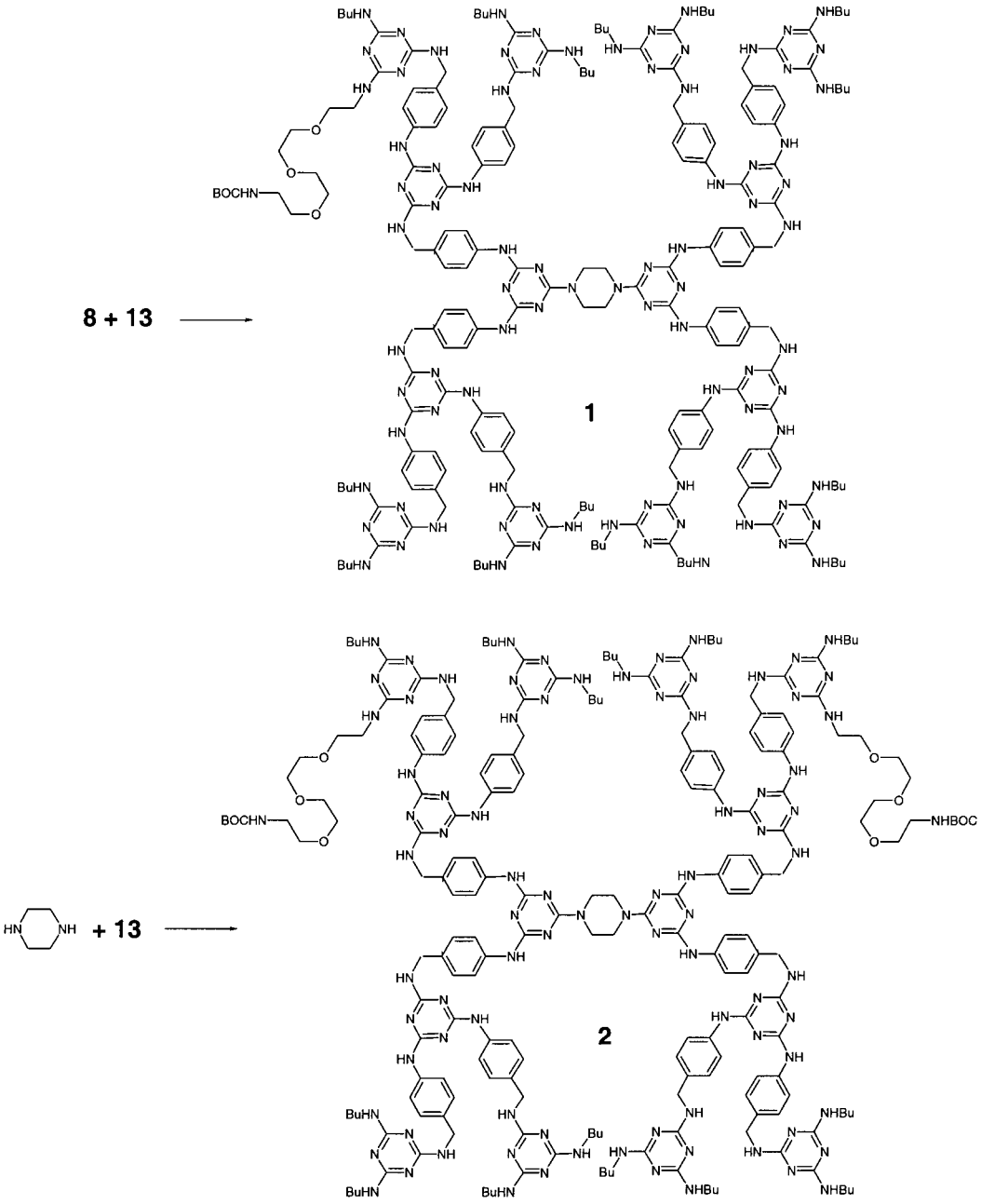
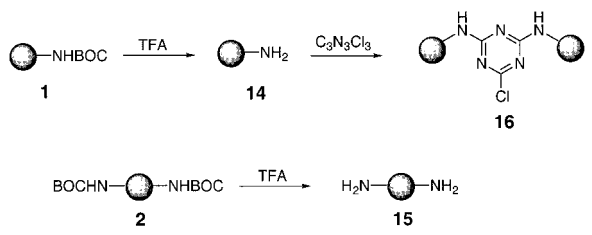
(19) For ^{15}N analyses of triazine rotamers, see: Amm, M.; Platzer, N.; Guilhem, J.; Bouchet, J. P.; Volland, J. P. *Magn. Reson. Chem.* **1998**, *36*, 587.

(20) Similar shifts in H-bonded melamine protons have been reported in hydrogen-bonded aggregates; for a general discussion, see ref 16. For Seto's initial report, see: Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *112*, 6409.

Scheme 5. Synthesis of the Dendrimers



Scheme 6. Manipulation of the Dendrimers



p-aminobenzylamine are also useful. In larger dendrons and dendrimers, lines corresponding to aromatic carbons without protons (typically the triazine) are sometimes absent. We continue to explore variable-temperature experiments and additional solvent(s) in an effort to identify these lines.

(b) Mass Spectrometry. A majority of the mass spectra reported were acquired using a MALDI-TOF instrument with trihydroxyacetophenone as the matrix. For the dendrons, a single line corresponding to the appropriate ion (and those for sodium and potassium adducts) is observed. For the dendrimers, the mass spectra reveal the desired ion, gas-phase aggregates of the desired ion, and lines corresponding to multiply charged adducts of the desired ion. Smaller lines attributed to fragment ions from the loss of the BOC group can be observed by altering the ionization conditions. The results for molecules **1** and **2**, as well as the other dendrons, are all very good.

In general, dendrimers based on melamine show unexpected behavior by mass spectrometry. While fast atom bombardment strategies typically provide excellent agreement between calculated and observed ions, MALDITOF gives broad lines that typically overestimate the MW value by approximately 0.05−0.1%. This disagreement increases with size and polarirty with the deprotected amines providing the largest errors. Unfortunately, as these molecules become larger, FAB no longer produces ions, and we are left to rely on isotope distributions that match the theortical distribution calculated for our molecules. As a result the mass spectra of molecules **14**−**16** display

Table 1. Combustion Analysis of Targets

compd	solvent	found (C, H, N)	calcd (C, H, N)	calcd (C, H, N + *n* solvent)
1	THF	61.22, 7.10, 29.20	61.08, 7.10, 29.82	61.17, 7.17, 29.29 (1 THF)
1	MeOH	60.45, 6.96, 29.42	61.08, 7.10, 29.82	60.70, 7.18, 29.35 (1 MeOH)
2	THF	60.28, 7.17, 27.57	60.46, 7.13, 28.60	60.66, 7.27, 27.66 (2 THF)
14	TFA	54.03, 6.20, 25.63	61.10, 7.07, 30.59	54.29, 6.02, 25.39 (7 TFA)
15	TFA	52.52, 5.96, 23.99	60.49, 7.09, 30.03	52.45, 5.82, 23.92 (9 TFA)
16	THF	60.58, 6.90, 29.74	60.70, 6.94, 30.69	60.80, 7.02, 30.14 (2 THF)

an error (100−600 ppm) outside the range of what is normally seen for small molecules. The isotope distribution pattern, however, matches the predicted values.

(c) Combustion Analyses. Combustion analyses of **1**, **2**, **14**, **15**, and **16** appear in Table 1. While none of the molecules give satisfactory analyses as pure analytes, differences can be rationalized by including solvent molecules from which the sample was derived.

(d) Size Exclusion Chromatography. We are surprised to find that the substitution of butyl groups for one or two Boc-amine groups dramatically affects our ability to obtain SEC traces for these materials. While all intermediates, **3**−**13**, elute off the column to provide clean SEC traces, none of the larger molecules incorporating this side chain (**1**, **2**, **14**−**16**) elute from the column. We prepared the all-butyl dendrimer (corresponding to reaction of **7** with **8**) to confirm that these polyether side chains influenced the behavior of these molecules on the column. Indeed, this molecule provides a trace consistent with dendrimers that present BOC-protected *p*-aminobenzylamine groups on the surface.

(e) Light Scattering. Light scattering confirms the expected difference in size between **1**, **2**, and **16**. The hydrodynamic diameters of **1** and **2** are measured to be 3.3 and 3.2 nm, respectively, corresponding to molecular weights of 4.4 and 4.1 kDa. The hydrodynamic radius calculated for the dimer, **16**, is 5.4 nm, corresponding to a molecular weight of 10.9 kDa. Computation corroborates these measurements.

(f) Atomic Force Microscopy. Dendrimers have been shown to spontaneously absorb to clean, atomically flat Au(111) surfaces allowing direct visualization with tapping mode(TM)-AFM.[21−23] The micrographs shown in Figure 1 include (a) the clean Au(III) surface before adsorbtion, (b) incubation of the surface with a solution of **1**, and (c) incubation with dimer **16**. The monoatomic steps present on the clean Au(111) surface are identifiable in the first panel. Treatment of the surface with THF provides an identical micrograph. The monolayers of dendrimers (lighter contrast) that appear in subsequent panels result from immersion of the Au for 30 s in a THF solution of the materials. Consistent with observations from other laboratories, monolayers formed over a 10^6-dilution range.[24] The apparent dispersion in the sizes of the dendrimers is due to either dendrimer aggregation, stacking, or differences in tip−dendrimer interactions which result in an apparent broadening of features on the surface.[25−27] This broadening becomes worse as the features approach the size of the end of the tip. All three panels were recorded with the same AFM tip to keep the tip broadening interaction similar in all three images.

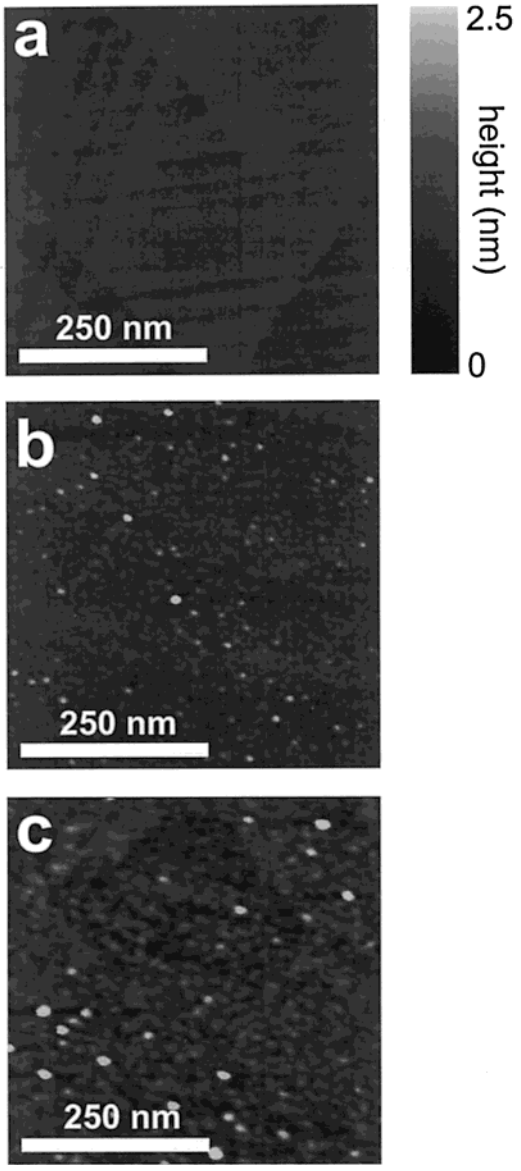


Figure 1. TM-AFM micrographs of (a) the clean Au(111) surface, (b) Au(111) surface modified with **1**, and (c) Au(111) surface modified with **16**. The lateral dimensions and height scale in all three micrographs are 500 × 500 and 2.5 nm, respectively.

The tip−dendrimer interaction does not affect the measured height of the features on the surface. Dendrimers typically appear flattened on the surface. Using Digital Instruments software, we determined that **1** has an average height of 1.4 nm, while **16** is larger with an average height of 1.9 nm. The widths of these molecules are exaggerated by the nature of the experiment, but are consistent with the differences in size: **1** has an average width of 11 nm, **16** has an average width of 21 nm.

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(26) Keller, D. J.; Franke, F. S. *Surf. Sci.* **1993**, *294*, 409.
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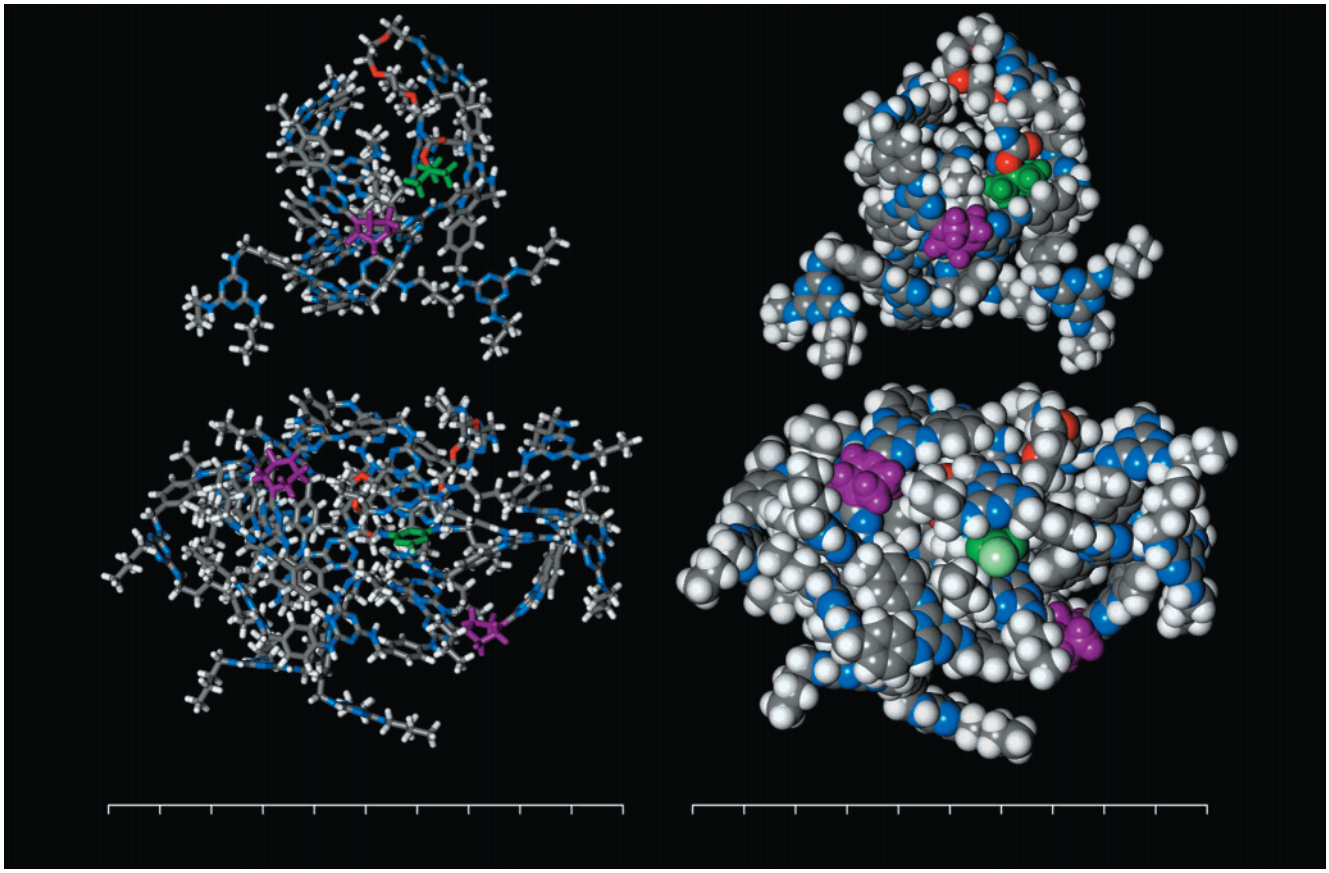

Figure 2. Computational models of the gas-phase structures of **1** and **16**. Piperazine cores are shown in maroon. The Boc-protected amine of **1** is shown in green. The triazine core of **16** is shown in green. The scale bar represents 5 nm.

(g) Computation. The gas-phase minimized structures of **1** and **16** are shown in Figure 2. These models serve to both ground our intuition and challenge our preconceptions of the structure of these molecules. Stacking of aromatic rings is responsible for the low-energy structures that were obtained starting from the fully extended, planar, butterfly-shaped structures (similar to that shown for **1** in Scheme 5).

Both molecules are small enough that the "core" piperazines (shown in maroon) of **1** and **16** and the Boc-protected amine of **1** (shown in green) are accessible to solvent in these models. However, the linker triazine of the dimer **16** (shown in green) is much less accessible to solvent. Calculations show that **1** has edge dimensions of 3 nm, and a radius of gyration of 1.05 nm. Dimer **16** is egg-shaped with dimensions of 3 nm and 5 nm. The calculated radius of gyration of **16** is 1.3 nm. As expected, these values are smaller than the dimensions observed by light scattering, and more consistent with the height of the dendrimers determined by TM-AFM.

Conclusions

The differential reactivity of triazines can be used to generate dendrimers with substoichiometric numbers of surface sites as demonstrated with the synthesis of **1** and **2**. The orthogonal, convergent route to these molecules proceeds in excellent yields with only traces of impurities that disappear upon purification of the deprotected targets. The surface sites can be manipulated as evident from the synthesis of the dimer, **16**, a molecule that represents the simplest "megamer" of a series of molecules that we are currently exploring.[28] These poly(dendrimer) assemblies, first described by Tomalia, offer opportunities to explore the synthesis and properties of molecules of a new length scale.[28,29] Tomalia's strategy, one that employs a cationic PAMAM dendrimer to recognize anionic PAMAM dendrimers before covalently cross-linking the assembly with a carbodiimide reagent, takes advantage of commercially available building blocks, and as such, is executed rapidly for the assemblies he has described. Our strategy differs somewhat from Tomalia's, however, in that we can manipulate the number and nature of the bonds between the dendrimer units. Ultimately, with synthesis, this strategy could afford greater control over structure and greater structural complexity.

Experimental Section

Computation. Computational results were obtained using the software package Cerius^2 4.2 by Accelrys Minimization and dynamics calculations in the gas phase were performed with the Open Force Field (OFF) program, using the pcff second generation force field.[30] Charges for the dendrimer were calculated using the QEq charge equilibration method. The dendrimer was initially minimized in the fully extended conformation. Constant volume and temperature (NVT) molecular dynamics (MD) calculations were then performed on the minimized structure via simulated annealing. The simulated annealing was carried out for 140.0 ps, over a temperature range of 300−1000 K, with $\Delta T =$ 50 K, using the Nosé temperature thermostat, a relaxation time of 0.1 ps, and a time step of 0.001 ps. Charges for the dendrimer were reequilibrated using QEq every 2.8 ps. The dendrimer was minimized after each anneal cycle of the 50 cycles performed. The minimized structures shown[31] in Figure 2 are the lowest energy structures found during the simulated annealing.

(28) Tomalia has proposed the term "megamer" to refer to any poly(dendrimer) assembly: Tomalia, D. A.; Uppuluri, S.; Swanson, D. R.; Li, J. *Pure Appl. Chem.* **2000**, *72*, 2343.

(29) Uppuluri, S.; Swanson, D. R.; Piehler, L.; Li, J.; Hagnauer, G. L.; Tomalia, D. A. *Adv. Mater.* **2000**, *12*, 796.

(30) Cerius^2 Forcefield-Based Simulations, September 1998, San Diego; Accelrys Inc., 2000.

AFM. Tapping-mode atomic force microscopy (TM-AFM) was used to characterize both the monomer and dimer dendrimer species. To perform the TM-AFM analysis the dendrimers were first adsorbed to Au(111) single-crystal surfaces. Au(111) single-crystal substrates were created by flame annealing and zone-refining Au wire to form 1.5−2.5 mm diameter beads containing single-crystal Au(111) facets.[32,33] The atomically smooth Au(111) surface serves as a flat reference plane onto which the dendrimer can be adsorbed. All Au(111) facets were imaged in the AFM prior to adsorption of the dendrimer to determine the structure of the Au. The Au was modified by immersion in dilute THF solutions of the dendrimer and dendrimer dimer for 30 s followed by rinsing in THF and drying under a stream of N_2. The gold bead was then mounted in the AFM with an Au(111) facet normal to the AFM tip. TM-AFM images were obtained in air using a Digital Instruments Nanoscope III (Santa Barbara, CA) fitted with a 200 mm *j* scanner. Tapping-mode cantilevers (NanoSensors, Wetzlar-Blankenfeld, Germany) had resonant frequencies between 260 and 280 kHz, force constants of 20−100 N/m, and tip apex radii of ∼10 nm. Images were acquired at 512 × 512 pixels at 1.0 Hz using a near-minimal contacting force. The resulting images were flattened and plane-fit using Digital Instruments software.

Dendrimer 1. Intermediate **8** (137 mg, 0.071 mmol) was dissolved in 3 mL of THF. To the solution **13** (149 mg, 0.071 mmol) and 0.1 mL of *N*,*N*-diisopropylethylamine (DIPEA) were added. The solution was bubbled with nitrogen and sealed in a Parr vessel. The mixture was heated to 80 °C and stirred for 36 h. Upon cooling and removal of the solvent, the residue was purified by column chromatography with CH_2Cl_2:CH_3OH (30:1, 20:1, 15:1) to give the product as a white solid (230 mg, 81%). ^{1}H NMR (300 MHz, DMSO) 8.94−9.13 (m, 12H), 7.66 (br, 24H), 7.50 (br, 1H), 7.23 (d, J = 12 Hz, 8H), 7.13 (br, 16H), 6.20−7.00 (br, 28H), 4.46 (br, 8H), 4.32 (br, 16H), 3.84 (br, 8H), 3.46 (br, 10H), 3.33 (br, 4H), 3.16 (br, 30H), 3.04 (m, 2H), 1.40 (br, 30H), 1.35 (s, 9H), 1.24 (br, 30H), 0.84 (br, 45H). ^{13}C NMR (75 MHz, DMSO) 166.41, 165.34, 164.77, 156.47, 139.31, 134.84, 134.32, 127.86, 120.47, 78.26, 70.41, 70.17, 69.86, 43,40, 32.27, 28.89, 20.29, 14.42. MS:[33] calcd 3991.94 (M^+); found (MALDITOF) 3992.82 ($M + H^+$). Hi-Res: Confirmed Isotope Distribution (+LSIMS).

Dendrimer 2. Intermediate **7** (1276 mg, 0.61 mmol) was dissolved in 10 mL of THF before DIPEA (0.15 mL) and piperazine (26.14 mg, 0.30 mmol) were added. The solution was bubbled with nitrogen, sealed in a Parr vessel, and heated to 80 °C with stirring for 36 h. Upon cooling and removal of the solvent, the residue was purified by column chromatography on silica gel with $CH_2Cl_2-CH_3OH$ (20:1, 16:1) to afford the product as a white solid (960 mg, 75%).^{1}H NMR (300 MHz, DMSO) 8.95−9.14 (m, 12H), 7.67 (br, 24H), 7.50 (br, 2H), 7.23 (d, J = 11.5 Hz, 8H), 7.14 (br, 16H), 6.20−7.00 (br, 28H), 4.47 (br, 8H), 4.34 br, 16H), 3.84 (br, 8H), 3.46 (br, 20H), 3.33 (br, 8H), 3.17 (br, 28H), 3.04 (m, 4H), 1.40 (br, 28H), 1.35 (s, 18H), 1.24 (br, 28H), 0.84 (br, 42H). ^{13}C NMR (75 MHz, DMSO) 166.40, 165.34, 164.77, 139.31, 134.86, 134.33, 127.87, 120.47, 78.24, 70.41, 70.20, 69.86, 43.45, 32.26, 28.88, 20.29, 14.42. MS: calcd 4211.01 (M^+); found (MALDITOF) 4212.63 ($M + H^+$), 4236.93 ($M + Na^+$), 4253.56 ($M + K^+$). Hi-Res: Confirmed Isotope Distribution (+LSIMS).

Intermediate 3. *n*-Butylamine (5.0 g, 68.36 mmol) was dissolved in 100 mL of THF. After cooling in an ice bath, triazine trichloride (6.30 g, 34.18 mmol) and DIPEA (15 mL) in 100 mL of THF were added dropwise. After 1 h the reaction mixture was warmed to room temperature and stirred for 12 h. Upon cooling and removal of the solvent, the solid was washed with CH_3OH-H_2O (2:1) to afford a white solid (8.28 g, 94%). ^{1}H NMR (300 MHz, DMSO) 7.78 (br, 1H), 7.66 (br, 1H), 3.20 (m, 4H), 1.46 (m, 4H), 1.23 (m, 4H), 0.87 (t, 6H). ^{13}C NMR (75 MHz, DMSO) 166.68, 166.02, 31.48, 20.18, 14.32. MS: calcd 257.76 (M^+); found (MALDITOF) 258.07 ($M + H^+$). HR-MS: calcd 258.1486 (M^+); found (+LSIMS) 258.1493 (M^+).

Intermediate 4. Intermediate **3** (5 g, 19.4 mmol) was dissolved in 100 mL of THF and 4-aminobenzylamine (7.10 g, 58.2 mmol) was added. Nitrogen was bubbled through the solution, the Parr vessel was sealed, and the mixture was heated to 70 °C for 12 h. After cooling to room temperature, the solid was filtered and solvent was removed. The residue was purified by column chromatography with CH_2Cl_2/CH_3OH (100:1, 50:1) to afford the product as a white solid (6.40 g, 96%). ^{1}H NMR (300 MHz, DMSO) 6.94 (br, 2H), 6.50−6.70 (br, 2H), 6.46 (d, J = 12 Hz, 2H), 6.22 (br, 1H), 4.88 (s, 2H), 4.22 (d, J = 7.5 Hz, 2H), 3.17 (br, 4H), 1.43 (br, 4H), 1.28 (m, 4H), 0.87 (t, 6H). ^{13}C NMR (75 MHz, DMSO) 166.45, 166.37, 147.80, 128.83, 114.26, 43.62, 32.32, 20.32, 14.45. MS: calcd, 343.45 (M^+); found (MALDITOF) 344.16 ($M + H^+$). HR-MS: calcd 344.2563 ($M + H^+$); found (+LSIMS) 344.2547 ($M + H^+$).

Intermediate 5. Intermediate **4** (4.40 g, 12.81 mmol) was dissolved in 100 mL of THF and cooled in an ice bath. Triazine trichloride (1.18 g, 6.40 mmol) and DIPEA were added in single portions. After 1 h the mixture was warmed to room temperature and stirring continued for 24 h. Upon removal of the solvent, the residue was purified by chromatography with CH_2Cl_2/CH_3OH (100:1, 50:1, 25:1) to give **5** (4.86 g, 95%). ^{1}H NMR (300 MHz, DMSO) 10.22−9.90 (br, 2H), 7.70 (br, 2H), 7.52 (d, J = 12 Hz, 4H), 7.23 (br, 4H), 7.00 (br, 2H), 6.22−6.90 (br, 4H), 4.37 (d, J = 7.50 Hz, 4H), 3.18 (br, 8H), 1.42 (br, 8H), 1.27 (m, 8H), 0.85 (t, 12H). ^{13}C NMR (75 MHz, DMSO) 169.00, 166.46, 164.63, 137.27, 128.06, 121.55, 43.44, 32.32, 20.36, 14.47. MS: calcd 798.50 (M^+); found (MALDITOF) 798.12 (M^+). HR-MS: calcd 820.4491 ($M + Na^+$); found (+LSIMS) 820.4456 ($M + Na^+$).

Intermediate 6. Intermediate **5** (2.50 g, 3.13 mmol) was dissolved in 100 mL of THF and *p*-aminobenzylamine (1.15 g, 9.40 mmol) was added. The resulting solution was bubbled with nitrogen, sealed in a Parr vessel, and stirred at 80 °C for 24 h. Upon cooling and removal of the solvent, the residue was purified by column chromatography with $CH_2Cl_2-CH_3OH$ (30:1, 20:1) to give a white solid (2.54 g, 92%). ^{1}H NMR (300 MHz, DMSO) 9.00 (s, 1H), 8.90 (s, 1H), 7.67 (d, J = 11 Hz, 4H), 7.38 (br, 2H), 7.15 (br, 4H), 7.01 (d, J = 12 Hz, 2H), 6.50 (d, J = 11.5 Hz, 2H), 6.22−7.00 (br, 5H), 4.92 (br, 2H), 4.35 (d, J = 7.5 Hz, 4H), 3.18 (br, 8H), 1.43 (br, 8H), 1.27 (m, 8H), 0.87 (t, 12H). ^{13}C NMR (75 MHz, DMSO) 166.40, 164.74, 147.90, 139.37, 134.73, 128.66, 127.97, 120.34, 114.43, 43.73, 32.25, 20.27, 14.37. MS: calcd 884.09 (M^+); found (MALDITOF) 884.24 (M^+).

Intermediate 7. Intermediate **6** (800 mg, 0.90 mmol) was dissolved in 50 mL of THF. Triazine trichloride (83.4 mg, 0.45 mmol) and DIPEA (0.4 mL) were added. The reaction mixture was stirred at room temperature for 24 h and then at 50 °C for 4 h. The solvent was removed and the residue was dissolved in $CH_2Cl_2-CH_3OH$ (30:1) and purified by chromatography with $CH_2Cl_2-CH_3OH$ (30:1) to give a white solid (756 mg, 89%). ^{1}H NMR (300 MHz, DMSO) 8.97−9.03 (br, 6H), 7.61 (br, 12H), 7.27 (br, 4H), 7.14 (br, 8H), 6.22−7.10 (br, 14H), 4.48 (br, 4H), 4.34 (br, 8H), 3.17 (br, 16H), 1.42 (br, 16H), 1.26 (m, 16H), 0.85 (br, 24H). ^{13}C NMR (75 MHz, DMSO) 168.10, 166.44, 164.78, 139.29, 137.60, 136.50, 134.88, 127.96, 121.57, 120.53, 43.64, 32.29, 20.31, 14.42. MS: calcd 1879.71 (M^+); found (MALDITOF) 1878.96 (M^+), 1900.97 ($M + Na^+$), 1916.99 ($M + K^+$).

Intermediate 8. Intermediate **7** (252 mg, 0.134 mmol) was dissolved in 6 mL of THF before piperazine (69 mg, 0.80 mmol) and DIPEA (0.1 mL of *N*,*N*-diisopropylethylamine) were added. The resulting solution was bubbled with nitrogen, sealed in a Parr vessel, and stirred at 80 °C for 24 h. Upon cooling and removal of the solvent, the residue was purified by column chromatography with $CH_2Cl_2-CH_3OH$ (20:1, 10:1, 5:1) to give a white solid (238 mg, 92%). ^{1}H NMR (300 MHz, DMSO) 8.93−9.07 (m, 6H), 7.64 (br, 12H), 7.50 (br, 2H), 7.23 (d, J = 11 Hz, 4H), 7.13 (br, 8H), 6.22−7.00 (br, 12H), 4.45 (br, 4H), 4.32 (br, 8H), 4.09 (br, 1H), 3.70 (br, 4H), 3.16 (br, 16H), 2.78 (br, 4H), 1.41 (br, 16H), 1.25 (br, 16H), 0.85 (br, 24H). ^{13}C NMR (75 MHz, DMSO) 166.46, 165.23, 164.67, 139.39, 134.82, 134.28, 127.81, 120.41, 49.27, 45.55, 43.68, 32.28, 20.30, 14.43. MS: calcd 1929.39 (M^+); found (MALDITOF) 1928.88 (M^+), 1950.90 ($M + Na^+$), 1966.88 ($M + K^+$).

Monoboc-Protected Diamine for the Synthesis of 9. To a solution of 5,8,11-trioxa-1,13-diamine (9.46 g, 49.27 mmol) in 30 mL of dioxane was added a 30 mL dioxane solution of di-*tert*-butyl dicarbonate (1.79 g, 8.21 mmol) dropwise. After the solution was stirred for 12 h at room temperature and solvent removed, 100 mL of water was added. The aqueous phase was extracted five times with 50 mL portions of dichloromethane. The organic phases were combined, extracted four

(31) Materials Studio 1.0; Accelrys Inc. 2000.
(32) Hsu, T.; Cowley, J. M. *Ultramicroscopy* **1983**, *11*, 239.
(33) Ross, C. B.; Sun, L.; Crooks, R. M. *Langmuir* **1993**, *9*, 632.

times with 50 mL of saturated NaCl solution, and dried over $MgSO_4$. The solid was filtered and dichloromethane was removed to provide the monoprotected diamine as a sticky oil (2.36 g, yield 98%). ^{1}H NMR (300 MHz, DMSO) 6.81 (t, 1H), 3.47 (m, 10H), 3.56 (m, 4H), 3.05 (m, 2H), 2.64 (br, 2H), 1.37 (s, 9H). ^{13}C NMR (75 MHz, DMSO) 156.26, 78.24, 73.60, 70.44, 70.20, 69.86, 67.03, 41.96, 28.89.

Intermediate 9. Triazine trichloride (1.46 g, 7.92 mmol) and DIPEA were dissolved in 10 mL of THF and cooled to −10 °C. Monoprotected diamine (2.32 g, 7.92 mmol) was added dropwise, and then the reaction mixture was stirred for 4 h at −10 °C. After warming to room temperature, the reaction was stirred for an additional hour. To this solution *n*-butylamine (0.79 mL, 7.92 mmol) was added. After the solution was stirred for 12 h, the solid was removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography (eluted with CH_2Cl_2−CH_3OH, 50:1, 35:1, 25:1) to give the product as a white solid (3.36 g, 89%). ^{1}H NMR (300 MHz, DMSO) 7.82, 7.61 (t, 1H), 7.74 (br, 1H), 6.70 (br, 1H), 3.49 (m, 10H), 3.37 (m, 4H), 3.20 (m, 2H), 3.07 (m, 2H), 1.45 (m, 2H), 1.28 (m, 2H), 0.87 (t, 3H).^{13}C NMR (75 MHz, DMSO) 169.90, 168.25, 166.13, 156.23, 78.21, 70.43, 69.87, 69.37, 69.12, 31.42, 28.85, 20.16, 14.28. MS: calcd 477.09 (M^+); found (MALDITOF) 477.172 (M^+), 499.13 ($M + Na^+$), 515.10 ($M + K^+$). HR-MS: calcd 477.2592 (M^+); found (+LSIMS) 477.2612 (M^+).

Intermediate 10. Intermediate **9** (4.07 g, 8.53 mmol) was dissolved in 20 mL of THF and 4-aminobenzylamine (3.12 g, 25.59 mmol) was added. The solution was bubbled with nitrogen, sealed in a Parr vessel, and stirred at 70 °C for 12 h. After cooling and removal of the solvent, the residue was purified by column chromatography (eluted with CH_2Cl_2−CH_3OH, 50:1, 35:1, 20:1) to give the product (4.56 g, 94%) as a sticky oil. ^{1}H NMR (300 MHz, DMSO) 6.94 (br, 2H), 6.76 (t, 1H), 6.66−6.10 (br, 3H), 6.46 (d, J = 12 Hz, 2H), 4.87 (s, 2H), 4.22 (d, J = 7.5 Hz, 2H), 3.49 (m, 10H), 3.35 (m, 4H), 3.18 (br, 2H), 3.06 (m, 2H), 1.43 (m, 2H), 1.37 (s, 9H), 1.26 (m, 2H), 0.87 (t, 3H). ^{13}C NMR (75 MHz, DMSO) 166.42, 156.27, 147.79, 128.85, 114.28, 78.28, 70.44, 70.20, 69.98, 69.87, 43.60, 32.27, 28.90, 20.31, 14.44. MS: calcd 562.68 (M^+); found (MALDITOF) 563.22 (M^+). HR-MS: calcd 585.3489 ($M + Na^+$); found (+LSIMS) 585.3510 ($M + Na^+$).

Intermediate 11. Triazine trichloride (1.31 g, 7.11 mmol) was dissolved in 50 mL of THF and the solution was cooled to −10 °C before **10** (4.0 g, 7.11 mmol) and DIPEA (1.5 mL) were added dropwise as a solution in THF. After the solution was stirred for 4 h at −10 to 0 °C and then at room temperature for 1 h, **4** (2.44 g, 7.11 mmol) was added in one portion. Stirring was continued at room temperature for 12 h. The solvent was removed and the residue was purified by chromatography with CH_2Cl_2−CH_3OH (50:1, 35:1, 25:1) to afford the product as a white solid (6.01 g, 83%). ^{1}H NMR (300 MHz, DMSO) 10.18 (br, 2H), 7.64 (br, 1H), 7.51 (d, J = 11.50, 4H), 7.21 (br, 4H), 6.20−7.10 (br, 6H), 4.36 (d, J = 8 Hz, 4H), 3.48 (br, 10H), 3.33 (br, 4H), 3.18 (br, 6H), 3.04 (m, 2H), 1.42 (br, 6H), 1.36 (s, 9H), 1.25 (m, 6H), 0.86 (t, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 168.90, 166.36, 164.47, 156.25, 137.34, 136.95, 128.06, 121.48, 78.26, 70.42, 70.17, 69.88, 43.62, 32.27, 28.89, 20.30, 14.42. MS: calcd 1017.73 (M^+); found (MALDITOF) 1017.26 (M^+), 1039.23 ($M + Na^+$), 1055.22 ($M + K^+$).

Intermediate 12. *p*-Aminobenzylamine (0.91 g, 7.43 mmol) was added to a solution of **11** (2.52 g, 2.48 mmol) in 50 mL of THF. After nitrogen was bubbled through the solution, the reaction was sealed in a Parr vessel and stirred at 80 °C for 24 h. After the solid was filtered and the solvent was removed, the residue was purified by column chromatography with CH_2Cl_2−CH_3OH (30:1, 25:1, 20:1) to give the product (2.43 g, 89%) as a white solid. ^{1}H NMR (300 MHz, DMSO) 9.00 (br, 1H), 8.90 (br, 1H), 7.67 (br, 4H), 7.38 (br, 1H), 7.14 (br, 4H), 7.00 (d, J = 11.5 Hz, 2H), 6.75 (br, 2H), 6.50 (d, J = 12 Hz, 2H), 6.20−6.65 (br, 5H), 4.91 (s, 2H), 4.34 (d, J = 8.0 Hz, 4H), 3.48 (br, 10H), 3.35 (br, 4H), 3.18 (m, 6H), 3.05 (m, 2H), 1.42 (br, 6H), 1.36 (s, 9H), 1.26 (m, 6H), 0.87 (m, 9H). ^{13}C NMR (75 MHz, DMSO) 166.47, 164.75, 155.93, 148.02, 139.40, 128.73, 128.02, 127.70, 120.39, 114.38, 78.29, 70.44, 70.20, 69.86, 43.82, 32.31, 28.93, 20.37, 14.50. MS: calcd 1103.32 (M^+); found (MALDITOF) 1103.31 (M^+), 1125.29 ($M + Na^+$).

Intermediate 13. Triazine trichloride (334 mg, 1.81 mmol) was dissolved in 50 mL of THF and cooled to −10 °C before **12** (2.0 g, 1.81 mmol) and DIPEA (0.4 mL) in 50 mL of THF were of added dropwise to the solution. The reaction mixture was stirred for 4 h at low temperature before being warmed to room temperature and stirred for another 2 h. Intermediate **6** (1.61 g, 1.81 mmol) was added to the solution in one portion. Reaction continued at room temperature for 12 h and then at 40 °C for 2 h. The solvent was removed and the residue was purified by flash chromatography (eluted with CH_2Cl_2−CH_3OH, 30:1, 25:1, 20:1) to give a white solid (3.17 g, 82%). ^{1}H NMR (300 MHz, DMSO) 8.99−9.04 (br, 6H), 7.67 (br, 12H), 7.29 (br, 4H), 7.16 (br, 8H), 6.20−7.05 (br,15H), 4.50 (br, 4H), 4.36 (br,8H), 3.48 (br, 10H), 3.40 (br, 4H), 3.18 (br, 14H), 3.07 (m, 2H), 1.42 (br, 14H), 1.27 (br, 14H), 0.86 (br, 21H). ^{13}C NMR (75 MHz, DMSO) 166.42, 164.77, 156.27, 139.28, 137.54, 136.29, 134.97, 127.95, 121.59, 120.49, 78.26, 70.42, 70.19, 69.88, 43.72, 32.28, 28.87, 20.31, 14.42. MS: calcd 2099.01 (M^+); found (MALDITOF) 2097.61 (M^+), 2119.57 ($M + Na^+$), 2135.53 ($M + K^+$).

All-Butyl Dendrimer. Intermediate **7** (51 mg, 0.027 mmol) was dissolved in 0.5 mL of THF and a drop of DIPEA and piperazine (1.2 mg, 0.0135 mmol) were added before the solution was bubbled with nitrogen, sealed in a Parr vessel, and heated to 80 °C with stirring for 36 h. After cooling and removal of the solvent, the residue was purified by column chromatography on silica gel with CH_2Cl_2−CH_3OH (25:1, 20:1) to afford the product as a white solid (37 mg, 73%). ^{1}H NMR (300 MHz, DMSO) 8.95−9.25 (m, 12H), 7.68 (br, 24H), 7.24 (d, J = 11.5 Hz, 8H), 7.16 (br, 16H), 6.20−7.00 (br, 28H), 4.46 (br, 8H), 4.34 (br, 16H), 3.70−3.90 (br, 8H), 3.17 (br, 32H), 1.38 (br, 32H), 1.25 (br, 32H), 0.85 (br, 48H). ^{13}C NMR (75 MHz, DMSO) 166.44, 165.35, 164.73, 139.31, 134.84, 134.28, 127.82, 120.41, 45.55, 43.66, 32.28, 20.31, 14.43. MS: calcd 3772.72 (M^+); found (MALDITOF) 3774.64 ($M + H^+$).

Monoamine 14. Dendrimer **1** (60 mg, 0.015 mmol) was dissolved in 2 mL of a 1:1 mixture of CH_2Cl_2 and TFA and the solution was stirred for 12 h. After removal of the solvent, the residue was purified by column chromatography with CH_2Cl_2−CH_3OH−NH_4OH (10:1:0.5) to give the product as a white solid (55 mg, 94%). ^{1}H NMR (300 MHz, DMSO) 9.20 (br, 12H), 8.00−8.80 (br, 28H), 7.71 (br, 24H), 7.23 7.24 (br, 24H), 4.45 (br, 24H), 3.55 (br, 12H), 3.27 (br, 30H), 2.98 (m, 4H), 1.48 (br, 30H), 1.27 (br, 30H), 0.88 (br, 45H). ^{13}C NMR (75 MHz, DMSO) 166.45, 165.35, 164.73, 139.59, 134.29, 133.70, 127.89, 120.46, 70.33, 69.70, 67.33, 43.78, 43.48, 31.87, 20.20, 14.32. MS: calcd 3891.76 (M^+); found (MALDITOF) 3894.93 ($M + H^+$).

Diamine 15. Dendrimer **2** (586 mg, 0.14 mmol) was dissolved in 10 mL of a 1:1 mixture of CH_2Cl_2 and TFA. The resulting solution was stirred at room temperature for 36 h. After removal of the solvent, the residue was purified by column chromatography with CH_2Cl_2−CH_3OH:NH_4OH (10:1:1) to give the product as a white solid (521 mg, 93%). ^{1}H NMR (300 MHz, DMSO) 8.97−9.13 (m, 12H), 7.92 (br, 2H), 7.66 (br, 24H), 7.51 (br, 2H), 7.32 (br, 12H), 7.22 (d, J = 12 Hz, 8H), 7.14 (br, 14H), 7.03 (br, 14H), 4.45 (br, 8H), 4.35 (br, 16H), 4.10 (br, 4H), 3.82 (br, 8H), 3.42−3.50 (m. 12H), 3.16 (br, 28H), 2.94 (m, 4H), 1.41 (br, 28H), 1.24 (br, 28H), 0.83 (br, 42H). ^{13}C NMR (75 MHz, DMSO) 166.46, 165.34, 164.74, 139.60, 139.37, 134.30, 133.70, 127.88, 120.47, 70.34, 69.69, 67.33, 43.78, 43,47, 31.87, 20.20, 14.32. MS: calcd 4010.79 (M^+); found (MALDITOF) 4012.90 (M^+), 4038.17 ($M + Na^+$).

Dimer 16. Monoamine **14** (40 mg, 0.01 mmol) and triazine trichloride (0.95 mg, 0.005 mmol) were dissolved in 0.5 mL of THF and 1 drop of DIPEA was added to the solution. The mixture was stirred at room temperature for 12 h and then warmed to 50° C for another 12 h. After removing the solvent the residue was purified by column chromatography with CH_2Cl_2−CH_3OH (25:1, 20:1) to yield a white solid (24 mg, 58%) that was analyzed by mass spectrometry. ^{1}H NMR (300 MHz, DMSO) 8.92−9.20 (m, 24H), 7.67 (br, 48H), 7.52 (br, 4H), 7.24 (d, J = 12 Hz, 16H), 7.16 (br, 32H), 6.50−7.00 (br, 54H), 4.47 (br, 16H), 4.35 (br, 32H), 3.84 (br, 16H), 3.47 (m, 32H), 3.17 (br, 60H), 1.40 (br, 60H), 1.24 (br, 60H), 0.84 (br, 90H). ^{13}C NMR (75 MHz, DMSO) 166.48, 166.10, 164.77, 139.35, 134.50, 134.30, 127.87, 120.49, 70.43, 70.24, 69.92, 43.68, 39.00, 32.23, 20.29, 14.41. MS: calcd 7895.00 (M^+); found (MALDITOF) 7900.46 (M^+).

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Note Added in Proof: Kawaguchi and Moore reported the synthesis of a monofunctionalized poly(arylacetylene) dendrimer bearing an aldehyde group (Kawaguchi, T.; Moore, J. S. *Polym. Prepr.* **1994**, *35*, 872). Takagi and coworkers have also reported on the synthesis of triazine dendrimers (Takagi, K.; Hattori, T.; Kunisada, H.; Yuki, Y. *J. Polym. Sci., Part A* **2000**, *38*, 4385).

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