J. Am. Chem. Soc. 1994, 116, 4537–4550

Phenylacetylene Dendrimers by the Divergent, Convergent, and Double-Stage Convergent Methods

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Received November 8, 1993[⊗]

Abstract: The divergent, convergent, and double-stage convergent methods for synthesizing phenylacetylene dendritic macromolecules are examined. Syntheses based on the divergent or double-stage convergent approaches are severely hampered by poor solubility of the growing macromolecules. The double-stage method is nonetheless successfully used in attaining a high molecular weight and apparently monodisperse dendrimer. Using the convergent approach, high molecular weight mono- and tridendrons are prepared. The repetitive chemistry employed for monodendron preparation includes palladium-catalyzed coupling of terminal acetylenes to an aromatic dibromide containing a trimethylsilyl (TMS) masked terminal acetylene. The synthetic cycle is completed by removing the TMS group under mildly basic conditions. These monodendrons can be coupled around a trifunctional core, such as triiodobenzene, yielding tridendrons. Solubility of both the mono- and the tridendrons is strongly dependent on the nature of the peripheral group. Qualitatively, solubility tends to plummet in the early stages of growth. Provided that growth can be sustained, however, this trend tends to reverse as the synthesis progresses. The best peripheral group of those examined thus far for maintaining adequate solubility of *both* mono- and tridendrons over this critical solubility minimum is di-*tert*-butylphenylacetylene. For dendrimers containing this peripheral group, solubility is high even in aliphatic hydrocarbon solvents at room temperature. When poor solubility does not hamper the synthesis, the limiting factors to sustaining growth become as much dependent on the ability to purify and characterize the product of the coupling reaction as on the chemistry of the coupling reaction itself. Size-exlusion chromatography is shown to be inadequate for differentiating partially coupled products from fully coupled tridendrons. This problem is believed to be especially severe for stiff dendritic macromolecules, since their molecular cross section is essentially constant once two of the three monodendrons have coupled to the central core. Unequivocal proof of structure for mono- and tridendrons through generation four ($C_{1134}H_{1146}$, mol wt 14 776) has been obtained using a combination of chromatographic techniques, isotope labeling studies, mass spectrometry, and multidimensional NMR experiments.

Introduction

Dendritic macromolecules[1] have attracted much attention as organic examples of well-defined nanostructures. These molecules are ideal model systems for studying how physical properties depend on molecular size and architecture. Unique properties and potential new applications are also possible from this novel class of macromolecules. Three major approaches known as the "divergent", "convergent", and "double-stage convergent" methods have been devised to synthesize dendrimers. The original divergent method, developed independently by Newkome[2] and Tomalia,[3] involves catenation of repeat units around a core. Repetition of this process allows rapid increase in the number of reactive functional groups on the periphery of the dendrimer. Advantages of the divergent approach are the rapid growth of the dendrimer series and an increase in mass of isolated products without significant steric inhibition at early generations. Limiting features of this method are the possibility of molecular imperfections at higher generations and the difficulty in selectively modifying peripheral functionality. The convergent approach developed by Hawker and Fréchet[4] and also by Miller and Neenan[5] begins with the synthesis of "monodendrons"[6] and finishes by coupling several of these segments around a multifunctional core. This approach offers such features as involvement of a very small number of reactive sites for growth, easy control of peripheral functionality,[4c] the ability to dramatically change molecular architecture by using different cores for a given monodendron,

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

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(2) (a) Newkome, G. R.; Yao, Z.-q.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003. (b) Newkome, G. R.; Yao, Z.-q.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849. (c) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176. (d) Newkome, G. R.; Nayak, A.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1992**, *57*, 358.

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(4) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (c) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1059. (d) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252.

(5) (a) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346. (b) Kwock, E. W.; Neenan, T. X.; Miller, T. M. *Chem. Mater.* **1991**, *3*, 775. (c) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(6) Mono-, di-, and tridendrons refer to dendritic architectures radiating outward from a point of singular, double, or triple connectivity, respectively. See: Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

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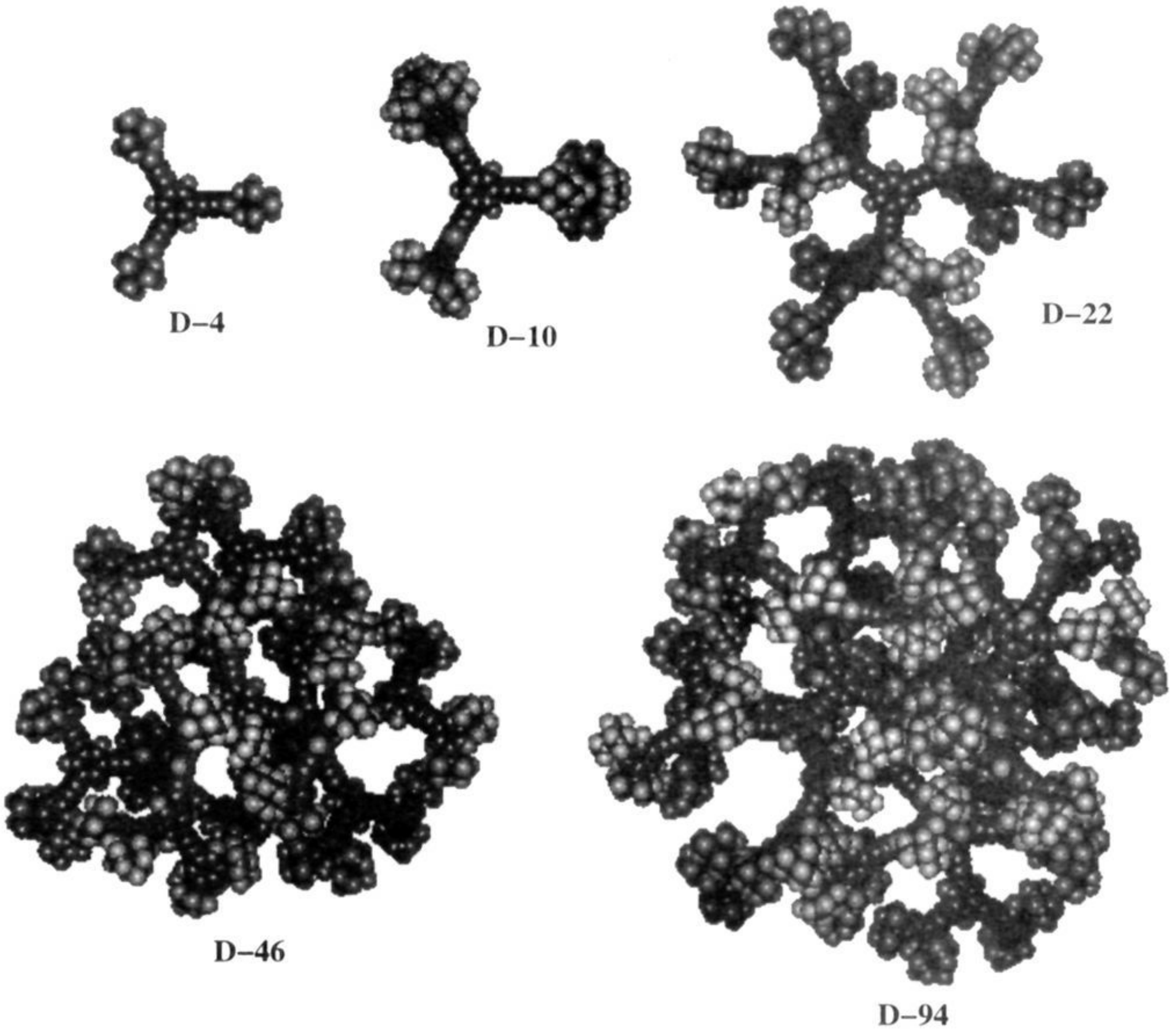


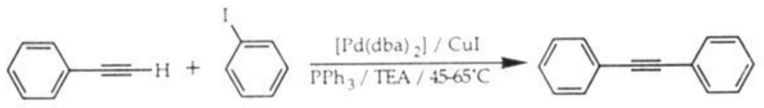
Figure 1. Space-filling models of phenylacetylene tridendrons **D-4**, **D-10**, **D-22**, **D-46**, and **D-94**.

and ease of purification and characterization of intermediates. One limitation of this approach is that the monodendrons are increasingly more susceptible to steric inhibition at the focal point, which tends to get internally buried. To overcome the problem of steric inhibition, Fréchet and co-workers recently reported the double-stage convergent approach, which employs a flexible, multifunctional dendritic core ("hypercore") in the final step of the synthesis.[4d] But, as in the case of the divergent method, the possibility of side reactions and/or imperfections due to incomplete conversion increases as the number of reactive sites in the hypercore increases.

To date, most of these synthetic methodologies were demonstrated by synthesizing dendritic molecules that involved repeat units possessing considerable flexibility.[7a] Conformational flexibility of these dendritic systems imparts a high degree of uncertainty to the overall three-dimensional structure, especially with regard to the size, shape and spatial location of functional groups.[7b,c] Greater definition in three-dimensional structure should be realized by constructing dendrimers from more rigid repeat units. Drawing upon analogies from stiff-chain linear polymers,[8] it is reasonable to expect that *shape-persistent* dendrimers may offer unique properties[9] compared with their flexible counterparts, although they may also bring new synthetic challenges such as poor solubility. Thus, it is of interest to test whether any of the known dendrimer methods are suitable for synthesizing stiff analogs.

Phenylacetylene repeat units were chosen as the base unit for our initial stiff dendrimers. The resulting hydrocarbons were envisioned to provide nonpolar molecular skeletons that possess limited degrees of conformational flexibility. Space-filling models of the first five members of the series are shown in Figure 1. It is apparent from these models that as the generation increases, the dendrimer takes on a more three-dimensional, spherical shape. The largest member of this series has a diameter of approximately 55 Å. This structure conforms well with the concept of a shape-persistent macromolecule.

The chemistry used to prepare phenylacetylene dendrimers is based on the well-established and high-yielding palladium-catalyzed cross-coupling reaction of terminal acetylenes and aryl halides (eq 1).[10] The necessary protecting group chemistry was also known at the start of this work. In fact, for phenylacetylene dendrimers, we had the advantage that suitable protecting schemes were available for either of the two partners of the cross-coupling reaction. The trimethylsilyl (TMS) group could be employed as a protecting group for terminal acetylenes[11] (eq 2), while 1-aryl-3,3-dialkyltriazenes are excellent masking groups for the aryl iodide bond[12] (eq 3). Although the dendrimer growth schemes mentioned above typically do not require protection of both



(1)

(2)

(3)

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(7) (a) One exception is the work by Miller et al., ref 5c. (b) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (c) Turro, N. J.; Barton, J. K.; Tomalia, D. A. *Acc. Chem. Res.* **1991**, *24*, 332–40.

(8) Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253.

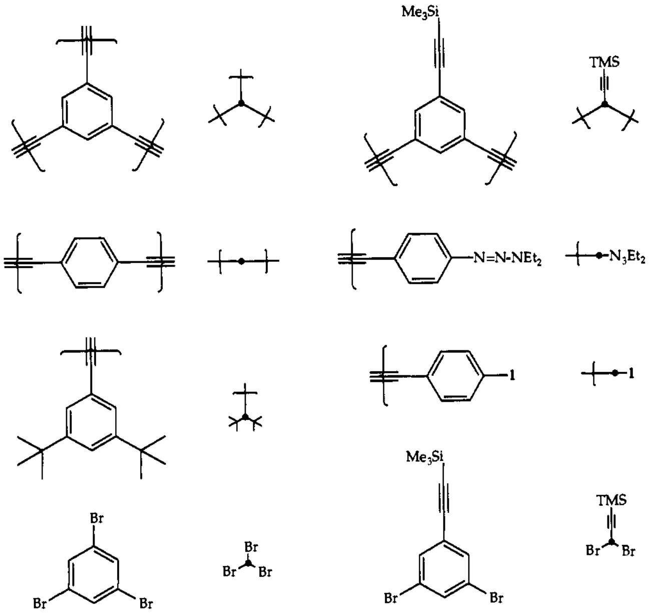
(9) For example, lyotropic liquid crystallinity has recently been reported for hyperbranched aromatic polyamides (Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947), and thermotropic liquid crystallinity has been reported for hyperbranched aromatic polyethers (Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843).

(10) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253. (c) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.

(11) (a) Eastmond, R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4591. (b) Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1965**, *4*, 217.

(12) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465.

Chart 1. Structure Key for Phenylacetylene Dendrimers



coupling partners, we have found it quite useful to have dual protecting schemes available, since this makes it possible to prepare the desired dendrimers by more than one synthetic route. The subtle advantages of one route versus another usually cannot be appreciated until the synthetic attempt is made (e.g., enhanced solubility, ease of separation from byproducts, etc.).

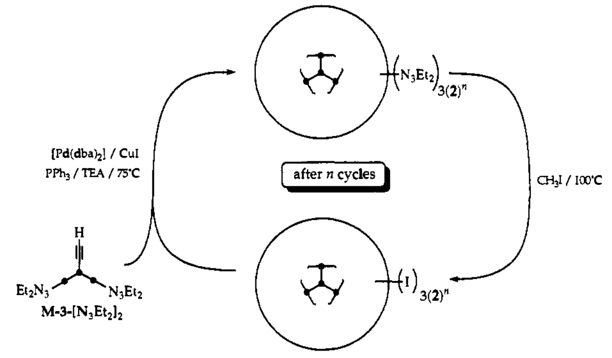
Here we describe the preparation of phenylacetylene dendritic macromolecules using the known dendrimer growth schemes described above. Comparison among these methods has shown that the convergent approach offers a distinct advantage over the other methods, especially in its ability to overcome the devastating problem of insolubility. Our initial efforts have been described in preliminary form.[13] Here we give a full account of the synthesis, purification, and characterization of phenylacetylene tridendrons.

In the discussion below, the various generations of phenylacetylene dendrimers will be designated by the descriptor **D-*x***, where *x* refers to the total number of phenylacetylene repeat units. Monomers of various sizes that are used in dendrimer syntheses will be designated as **M-*x*-[G]*$_y$*** and cores as **C-*x*-[G]*$_y$***, where *x* and *y* are the number of phenylacetylene units and the number of functional groups, G, respectively. Monodendrons will be designated by the descriptor **W-*x*-G**, in which *x* refers to the total number of phenylacetylene units and G refers to the functionality at the monodendron focal point. Throughout the paper we will use a simplified format to represent chemical structures. The structure key we use is given in Chart 1, where phenylene rings are represented by the symbol ● and acetylene linkages between rings by solid lines. The angle defined by phenylene ring connectivity is indicated by the angle between solid lines made at the ● vertex. Functional groups are indicated as shown in Chart 1.

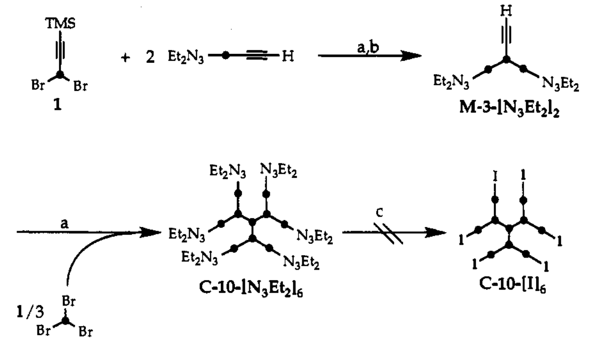
Results and Discussion

Divergent Method. Scheme 1 illustrates the repetitive chemistry we used in attempting to prepare triconnected phenylacetylene dendrimers by the divergent approach. In this synthetic plan, we chose the aryl iodide coupling partner as the reactive peripheral functionality rather than the acetylene partner in order to avoid dendrimers having a multiterminal acetylene periphery which may be unstable. Thus, this route required a monomer functionalized with a single terminal acetylene and a pair of masked aryl iodide groups. An easily prepared monomer meeting these requirements is **M-3-[N$_3$Et$_2$]$_2$**, whose synthesis is shown in Scheme 2. The divergent synthesis begins (n = 0) from a trifunctional core. Each cycle involves unmasking the peripheral aryl iodides followed by coupling to the acetylene monomer. With each round of synthesis, the number of peripheral groups doubles and the number of repeat units added in the n^{th} cycle is $3(2^n)$. The process is, in principle, repeated until the desired molecular size has been obtained.

Scheme 1. Repetitive Chemistry Used To Prepare Phenylacetylene Dendrimers by the Divergent Method



Scheme 2. Attempted Divergent Synthesis of Phenylacetylene Dendrimers[a]



[a] (a) [Pd(dba)$_2$]/PPh$_3$/CuI/TEA/80 °C. (b) KOH/MeOH/CH$_2$Cl$_2$. (c) CH$_3$I/100 °C.

Scheme 2 shows the results of our attempt to execute this divergent approach. Our initial target was the hexaiodo core, **C-10-[I]$_6$**, which can be considered as a first-generation tridendron. Coupling the bis(triazene) monomer **M-3-[N$_3$Et$_2$]$_2$** with tribromobenzene led to the hexatriazene **C-10-[N$_3$Et$_2$]$_6$** in 76% yield. This product was soluble in a variety of solvents and was fully characterized by NMR and elemental analysis. Attempted conversion to the hexatriazene to the corresponding hexaiodide, however, led to a product which showed virtually no solubility in any common solvents. Consequently, purification and characterization efforts were severely hampered. The only characterization data obtained on this compound were from elemental analysis, which suggested the presence of impurities. At this point we considered modifying the repeat unit to enhance solubility. Frustrated by the problem of insolubility at such an early stage in the synthesis, however, we elected to investigate other synthetic approaches as described below.

Convergent Method. In recognition of the limitations in the divergent approach, Fréchet and Hawker[4a] and Miller and Neenan[5a] developed a convergent route for preparing dendritic macromolecules whereby the synthesis begins from the periphery of the dendrimer. The process begins by reacting 2 equiv of species that will form the dendrimer's peripheral groups with a difunctional monomer, yielding the generation zero monodendron. Repetition of this process results in a homologous series of monofunctional macromolecules. The last step involves coupling monodendrons of a given generation to a multifunctional core, thus generating a multidendron.[6]

Two characteristics of the convergent method might be expected to improve solubility. First, the growing monodendrons possess

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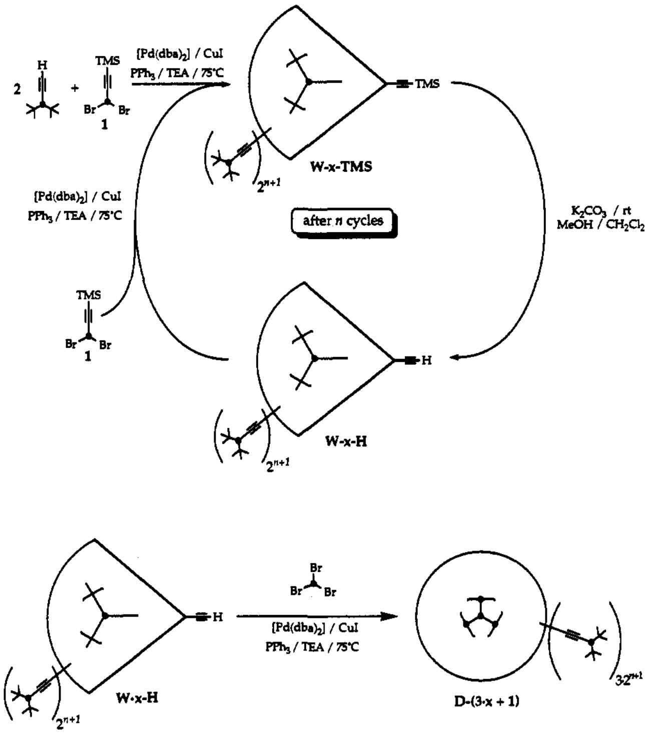
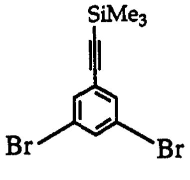
(13) (a) Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893. (b) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246.

Scheme 3. Chemistry Used To Prepare Phenylacetylene Dendrimers by the Convergent Method



lower symmetry than the dendrimers grown by the divergent route. Second, it is possible to enhance solubility by attaching pendant groups onto the periphery of the dendrimers. Unlike the divergent route, these groups will be present throughout the entire synthesis.

3′,5′-Dibromo-2-phenyl-1-(trimethylsilyl)acetylene (**1**) was selected for the convergent synthesis. This monomer is easily



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prepared in good yield from commercially available tribromobenzene according to a modified literature procedure.[13a,14] Scheme 3 illustrates the chemistry used in preparing phenylacetylene dendrimers by the convergent approach. The synthesis starts by preparing a series of monodendrons using the repetitive process shown at the top of Scheme 3. Entry into this repetitive cycle involves coupling aromatic dibromide **1** with 2 equiv of a terminal alkyne ($n = 0$ at the completion of this step). Following this initial coupling step, the TMS group is removed, leaving a terminal alkyne at the monodendron focal point. Two equivalents of this alkyne are then coupled with monomer **1** to give the first generation ($n = 1$) product, **W-7-TMS**, having four peripheral units. In principle, this repetitive process can be continued until the desired monodendron size has been obtained. At this point, the monodendrons can be deprotected and coupled to a core such as tribromobenzene, as shown at the bottom of Scheme 3.

The first peripheral group tested was phenylacetylene. Coupling 2 equiv of phenylacetylene to monomer **1** generated the zero-generation monodendron in 74% yield. This product was deprotected under basic conditions and then coupled to the monomer **1** to provide the first-generation monodendron in 67% yield. Attempts to synthesize and purify the second-generation monodendron by this process, however, were unsuccessful. In fact, the major product isolated from column chromatography was the half-reacted product in which only 1 equiv of the previous generation monodendron coupled to **1**. The reason for this failure is not entirely clear. Poor solubility is one possible cause. To increase solubility, 4-methoxyphenylacetylene peripheral groups were then tested. Indeed, the result was encouraging: a 22% yield of the second-generation monodendron was obtained.

Table 1. Yield[a] Data of Phenylacetylene Mono- and Tridendrons

wedge or dendrimer	generation[b]	synthetic method[c]	isolated yield[d] (%)
W-3-TMS	0	C	93
W-7-TMS	1	C	80
W-15-TMS	2	C	51
W-31-TMS	3	C	21
D-4	0	C	77[e]
D-10	1	C	73[e]
D-22	2	C	54[e] (84[f])
D-46	3	C	46[e] (54[f])
D-94	4	C	37
D-106	4	DS	36

[a] Yield data are for the cross-coupling reaction. [b] See text for definition. [c] C = convergent; DS = double-stage. [d] All compounds give single, narrow peaks by SEC and are homogeneous by TLC. [e] Using 1,3,5-tribromobenzene. [f] Using 1,3,5-triiodobenzene.

To select more suitable peripheral groups, several other terminal acetylenes were tested, including 4-*tert*-butylphenylacetylene and 3,5-di-*tert*-butylphenylacetylene. These terminal alkynes enhanced solubility and gave higher yields for the second-generation monodendron compared to 4-methoxyphenylacetylene. Table 1 shows yield data for monodendrons synthesized with 3,5-di-*tert*-butylphenylacetylene peripheral groups, all of which were soluble in a wide range of organic solvents. It should also be noted that the corresponding monodendrons containing 4-*tert*-butylphenylacetylene are also soluble in common organic solvents. However, when these monodendrons were coupled to prepare didendrons or tridendrons, poorly soluble products resulted. In contrast, mono- *and* tridendrons containing di-*tert*-butylphenylacetylene peripheral groups displayed excellent solubility, even in *n*-alkanes. Thus, all of the dendritic molecules described below are based on the di-*tert*-butylphenylacetylene peripheral group.

Figure 2 shows the series of phenylacetylene monodendrons prepared using the convergent route (Scheme 3). Note that some of the bond lengths have been increased for clarity. The synthesis was carried out successfully through generation $n = 3$ (**W-31-TMS**). Attempts to prepare **W-63-TMS** were not successful (see below).

All monodendrons were purified by standard silica gel chromatography. Since the solubilities of all of these products were quite high even in aliphatic hydrocarbon solvents, chromatographic separation was straightforward, although band broadening became more severe as the molecular weight increased. Attempts to decrease band broadening by using a more polar solvent composition gave rapid elution with no separation. The only significant impurity detected was a small amount of diacetylene obtained by oxidative dimerization of the starting monodendron. It became increasingly difficult to separate the diacetylene byproduct from the corresponding TMS-protected monodendron with each generation. For a particular coupling reaction, the byproduct differs from the desired monodendron by only a single aromatic ring. For example, in the case of the 31-mer monodendron mentioned above, the 30-mer diacetylene byproduct has to be carried along in the synthesis since preparative separation is virtually impossible. Only by ^{1}H NMR spectroscopy is it possible to identify the presence of the two components. Similar behavior is observed for previous members of the series (e.g., the 7-mer monodendron is contaminated by its 6-mer diacetylene byproduct; the 15-mer monodendron is contaminated by its 14-mer diacetylene byproduct). This impurity could be

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(14) (a) Trumbo, D. L.; Marvel, C. S. *J. Polym. Science* **1986**, *24*, 2311. (b) Bumagin, N. A.; Ponomarev, A. B.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1561.

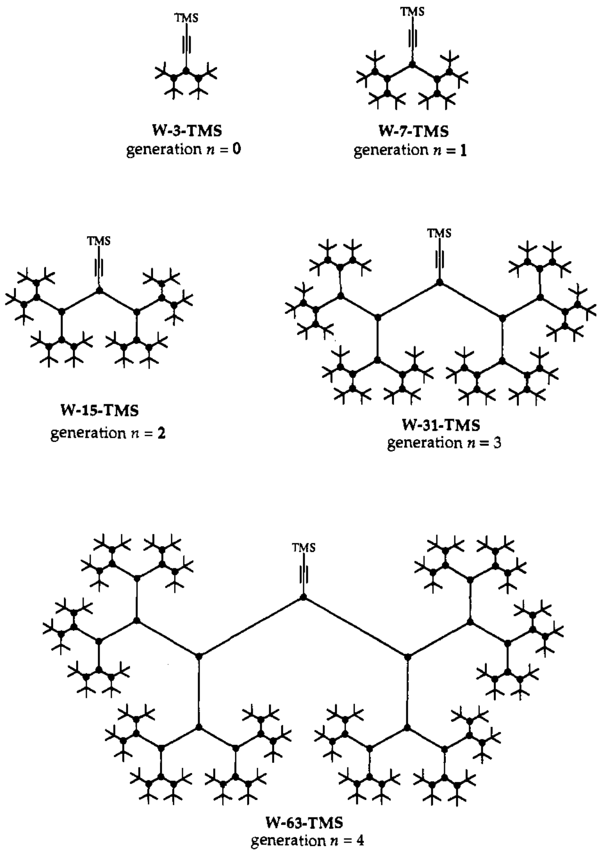

Figure 2. Monodendrons prepared by the convergent method.

removed by doing careful low-pressure silica gel chromatography or gravity chromatography several times. This separation was only performed for characterization purposes on small quantities of materials. From a practical standpoint, it has proven advantageous to simply carry the unreactive diacetylene to the next step, since removal of this side product can easily be accomplished at that stage.

The purified monodendrons were characterized by a combination of elemental analysis, thin-layer chromatography (TLC), size-exclusion chromatography (SEC), and ^{1}H and ^{13}C NMR. TLC and SEC could easily resolve contiguous members of the series. By either of these methods, no evidence for contamination with members of preceding generations could be found. As expected, the R_f values decrease as the size of the monodendron increased. Tailing also become more severe with increasing generation, making it increasingly difficult to check for the presence of the diacetylene dimer side product. Molecular weight data obtained by SEC calibated with narrow polystyrene standards are shown in Table 2. The observed molecular weights can be seen to increase smoothly as expected, roughly doubling in size with each generation. All of the monodendrons give very narrow and symmetrically-shaped SEC traces (M_w/M_n < 1.03). However, it is doubtful that SEC is capable of resolving the presence of diacetylene side product from the desired monodendron, especially at the low levels of diacetylene expected.

Elemental composition of the monodendrons was determined by combustion analysis, and the observed composition is very close to the expected value (in most cases within ±0.2%). For the series of monodendrons shown in Figure 2, the changes in carbon composition from one generation to the next are at least 0.74%, which is greater than the anticipated ±0.2% sensitivity of combustion analysis. Nonetheless, the calculated change is small enough that the data cannot be used to distinguish a pure monodendron from a mixture of monodendrons of contiguous generations. Moreover, the possibility of contamination by a small quantity of the diacetylene self-coupling byproduct would not be revealed by combustion analysis.

Table 2. Molecular Weight and Size Data of Mono- and Tridendrons Prepared by the Convergent and Double-Stage Methods

wedge or dendrimer	mol formula	mol wt calcd	mol wt obsd[e]	mol wt obsd[f]	M_w/M_n[f]	relative size[g] (Å)
W-3-TMS	$C_{43}H_{54}Si$	598[a]		690	1.03	6
W-7-TMS	$C_{91}H_{102}Si$	1222[a]		1750	1.02	11
W-15-TMS	$C_{187}H_{198}Si$	2470[a]		3550	1.02	17
W-31-TMS	$C_{379}H_{390}Si$	4966[a]		6100	1.02	23
D-4	$C_{54}H_{69}$	714.5164[b]	714.5237	1050	1.03	8
D-10	$C_{126}H_{138}$	1651.080[b]	1651.064	2610	1.02	14
D-22	$C_{270}H_{282}$	3631.112[c]	3631.063	4780	1.02	20
D-46	$C_{558}H_{570}$	7276.69[d]	7276.00	7690	1.03	27
D-94	$C_{1134}H_{1146}$	14 775.6[d]	14 775.2	9100	1.03	29
D-106	$C_{1230}H_{1194}$	15 954[a]		11 200	1.03	33

[a] Nominal mass. [b] Molecular mass of the all-^{12}C molecular ion. [c] Molecular mass of the all-^{12}C and 1-^{107}Ag molecular ion. [d] Weighted average molecular ion mass. [e] Determined by mass spectrometry (see Experimental Section). [f] Determined by size-exclusion chromatography relative to narrow molecular weight polystyrene standards. [g] Relative size refers to the corresponding radius of gyration of polystyrene at the same SEC elution volume. For polystyrene in THF at 20 °C, the radius of gyration follows the empirical relationship given by $R_g = 0.137M^{0.589}$ Å (see Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979; pp 35, 43–46).

Proton NMR was found to be very useful for the characterization of the monodendrons. Obvious features of these spectra are a single, sharp *tert*-butyl proton resonance, the singlet resonance corresponding to protons on the TMS focal point group, and several aromatic resonances. The integral ratio of the focal point to peripheral group functionality is, in principle, an excellent way to track the growth of the monodendron series. For the monodendrons shown in Figure 2, the *tert*-butyl (δ 1.42) and TMS (δ 0.35) singlets are convenient resonances for monitoring this ratio. The observed ratios are in good agreement with their expected values, so long as precautions are taken to provide quantitative integrated intensities.[15] The error of the measurement increases at higher generations due to the diminishing intensity of the TMS resonance, which becomes significant relative to the base-line drift. Nonetheless, since the calculated integral ratio doubles in proceeding from one generation to the next, and since the error is significantly smaller than the change in this ratio, the observed integral ratios support the expected compositions. However, given the precision of the measurement, the possibility of contamination by proceeding members of the series, or more likely, by diacetylene dimer cannot be unambiguously ruled out by the integration data alone.[16]

The aromatic regions of the ^{1}H NMR spectra contain a wealth of information provided sufficient chemical shift dispersion can be realized. Through variation of NMR solvent and temperature, it was often possible to find conditions such that all resonances could be unambiguously assigned. Aromatic solvents such as benzene-d_6 gave significantly better dispersion than $CDCl_3$. Most of the aromatic resonances in **W-31-TMS** could be resolved using benzene-d_6 as solvent. By varying the temperature, it was often possible to obtain additional chemical shift dispersion. Under carefully selected conditions, all five of the expected AB_2 (almost AX_2) spin systems can be located, and the integration (see Figure 3) matches that expected for this structure. Two-dimensional NMR experiments also proved to be extremely useful in elucidating the structures of these monodendrons, especially in higher generations, where overlap becomes more severe. COSY-45 and *J*-resolved spectroscopy proved to be a powerful combination for identifying correlations within common spin systems and multiplicity of resonances, respectively. For example, these

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(15) The difficulties and necessary precautions in obtaining quantitative ^{1}H NMR intensity measurements have been taken into consideration; see for example: Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: Oxford, England, 1987; pp 168–172. From our experience, for two resonances that differ greatly in intensity, as is the case with the higher generation monodendrons, the biggest contribution to integration error is the quality of the spectral base line.

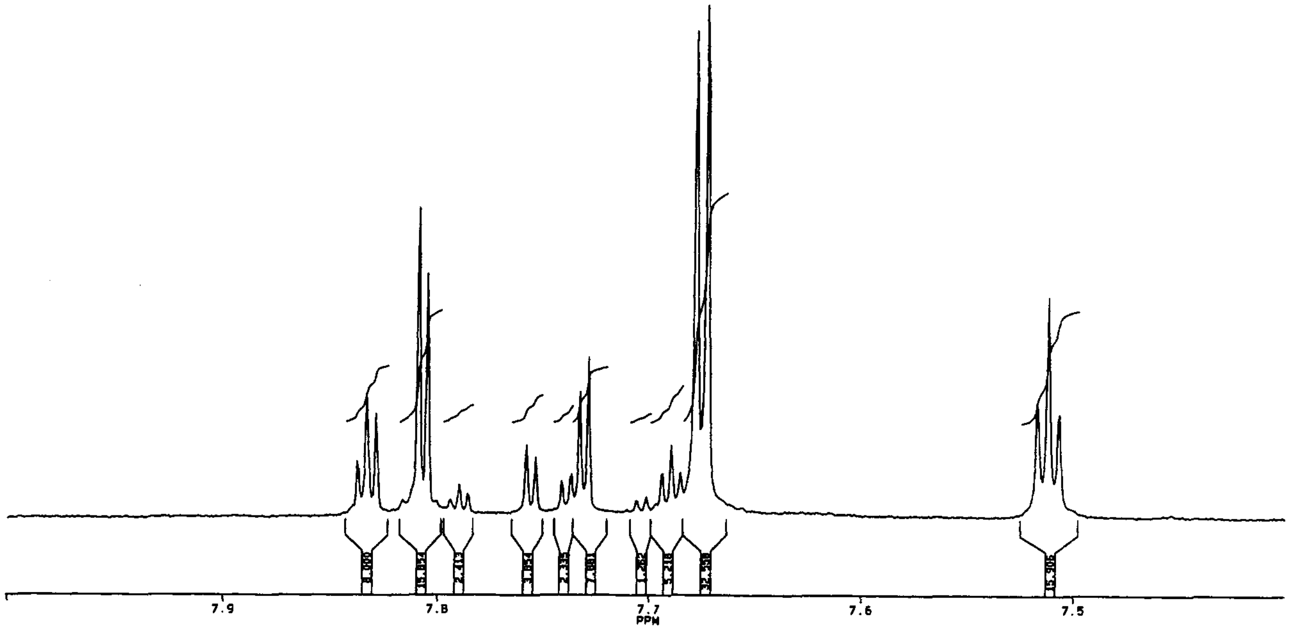


Figure 3. Integration of the aromatic region of ^{1}H NMR spectra of **W-31-TMS** in benzene-d_6 (360 MHz, 300 K).

techniques confirmed that the overlapped region around δ 7.67–7.71 in Figure 3 consisted of one doublet and two triplets.

Attempted preparation of the fourth-generation monodendron **W-63-TMS** from monomer **1** and **W-31-H** did not generate the expected product. The product that could be isolated by column chromatography was the oxidative dimer of the starting monodendron. Proton NMR and elemental analysis confirm this result (e.g., no trimethylsilyl protons were observed). The reason for the low reactivity of the cross-coupling reaction versus the self-coupling reaction is unknown at this time. In general, the amount of diacetylene product was observed to increase in higher generations, which could reflect steric crowdedness around the focal point of the monodendron. For the highest generations, diacetylene byproduct formation is significant even when molecular oxygen is rigorously excluded. For example, in the synthesis of **W-31-TMS**, ca. 25–35% of the observed product was diacetylene dimer (determined by ^{1}H NMR).

As illustrated at the bottom of Scheme 3, the deprotected monodendrons in Figure 2 can be coupled to tribromo- or triiodobenzene to give the tridendrons shown in Figure 4. The size of these tridendrons as a function of generation follows the recursive relationship shown in eqs 4 and 5, where x_n is the total number of phenylacetylene monomers in a tridendron of generation n. Thus, the generation zero dendrimer contains four

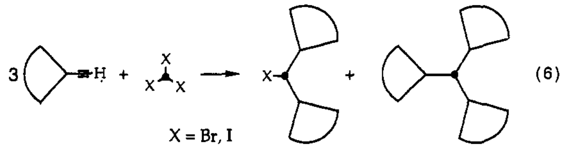
$$x_0 = 4 \qquad (4)$$

$$x_{(n+1)} = 2x_n + 2 \qquad (5)$$

phenylacetylene monomers, and it is denoted as **D-4**. The later generations of dendrimers are denoted as **D-10**, **D-22**, **D-46**, and **D-94** containing 10, 22, 46, and 94 phenylacetylene units, respectively.

These dendrimers were purified by silica gel chromatography, and all of the products showed excellent solubility in common organic solvents including n-alkanes. The major impurities were again the diacetylene dimer of the monodendron wedge and residual catalyst. However, in the case of the tridendrons, the diacetylene byproduct was usually well resolved on silica gel from the desired product, especially in the early generations. To follow the progress of the coupling reaction, TLC was usually capable of differentiating the starting monodendron from the desired tridendron.

The possibility of partially coupled products, as suggested in eq 6, was always considered as a defect structure. To test this possibility, the TLC elution behavior of the products from the tridendron coupling reaction was compared to the behavior of monodendrons of the same generation as the desired tridendron (i.e., monodendrons one generation higher than the starting monodendrons). For a given generation, these monodendrons have the same number of phenylacetylene units as the monobromo intermediate shown in eq 6, differing from this intermediate only in the focal point functionality (Br vs TMS acetylene). As noted above, R_f values for the monodendrons were found to correlate well with the number of aromatic rings, and so this comparison should be reasonable. As an example, the synthesis of **D-46** was attempted by coupling **W-15-H** to tribromobenzene. The resulting product was then eluted against **W-31-TMS**, a monodendron that contains the same number of phenylacetylene units as the product that would result by coupling 2 equiv of **W-15-H** to tribromobenzene. It was found that **W-31-TMS** had an intermediate R_f value between the observed reaction product and **W-15-H**. In some instances it was possible to observe an intermediate in the coupling reaction that had an R_f value between the final product and the starting monodendron. We presumed this intermediate to be the monobromide species.



X = Br, I

Using 1,3,5-tribromobenzene as the core, tridendron yields were observed to drop off rapidly as a function of generation (see Table 1). In fact, the fourth-generation tridendron, **D-94**, could not be prepared from tribromobenzene and **W-31-H**. The only major product observed under these conditions was the diacetylene byproduct from oxidative dimerization. To overcome the low

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(16) For the monodendrons in Figure 2, the calculated ratio, R', of *tert*-butyl to total aromatic protons as a function of generation, n, goes as,

$$R' = \frac{6(2^{n+1})}{2^{n+2} - 1} \qquad \text{(i)}$$

For generations 0, 1, 2, and 3, the value of R' = 4.0, 3.43, 3.2, and 3.10, respectively. As $n \to \infty$, R' approaches the same limiting value of 3.0 as is found for the tridendrons (see below). For the diacetylene self-coupling byproduct, the calculated ratio, R'', of *tert*-butyl to total aromatic protons as a function of generation, n, goes as,

$$R'' = \frac{6(2^{n+1})}{2^{n+2} - 2} \qquad \text{(ii)}$$

which is nearly identical to eq i above. Once again, R'' approaches the limiting value of 3.0 as $n \to \infty$.

3 **W-1-H** + 1,3,5-tribromobenzene → **D-4**

3 **W-3-H** + 1,3,5-tribromobenzene → **D-10**

3 **W-7-H** + 1,3,5-triiodobenzene → **D-22**

3 **W-15-H** + 1,3,5-triiodobenzene → **D-46**

3 **W-31-H** + 1,3,5-triiodobenzene → **D-94**

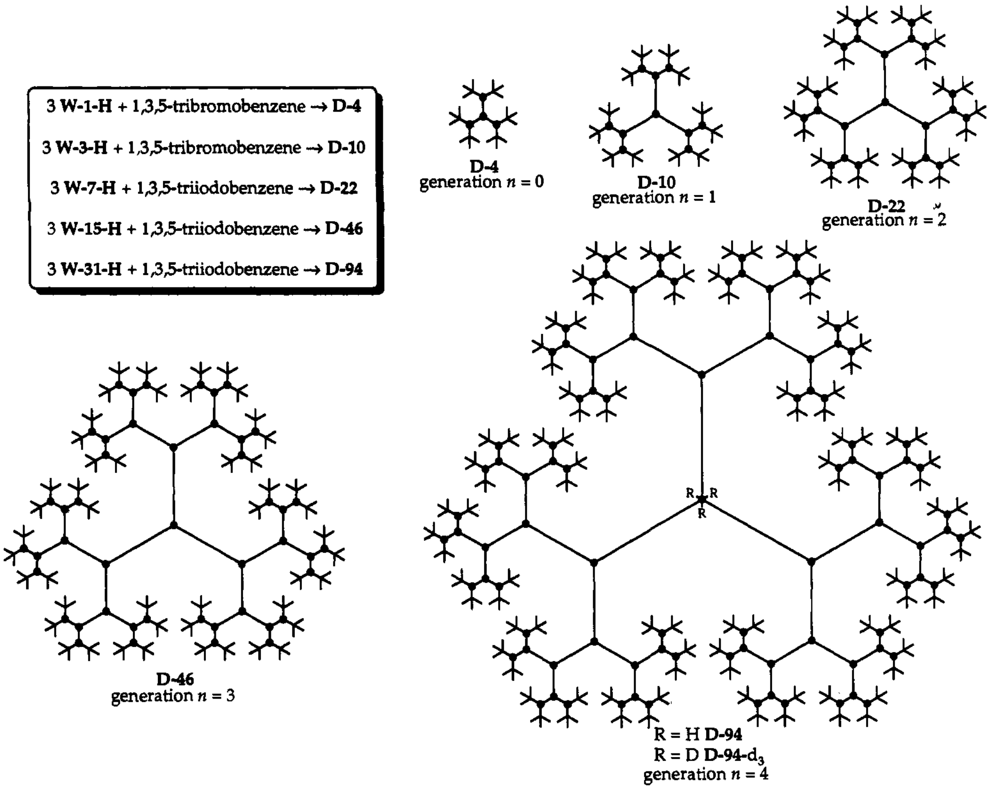

Figure 4. Tridendrons prepared by the convergent method.

reactivity of tribromobenzene, 1,3,5-triiodobenzene was examined as the core. Interestingly, using this core reaction, conditions could be found so as to yield **D-94**. Aryl iodides allow the coupling reaction to be performed at lower temperatures. Long reaction times are required under these conditions, but the yield of the cross-coupling product is higher (Table 1). As molecular weight increases, it becomes necessary to use substantially larger quantities of catalyst (e.g., 10 mol % based on terminal acetylene instead of the more usual 2 mol %). Importantly, whenever large quantities of catalyst are used, it is essential to run the reaction at low temperature (35–40 °C) for longer periods of time (≥48 h). At higher temperatures (e.g., 80 °C) with large catalyst concentrations, side reactions prevail, leading to unidentified high molecular weight products and essentially none of the desired dendrimer.

Molecular weight and size data for the dendrimers as determined by SEC and mass spectrometry are included in Table 2. Examination of the SEC molecular weight data shows that the observed molecular weight smoothly rises with each generation. Moreover, all of the coupling products have narrow and symmetrically-shaped elution curves with polydispersities (M_w/M_n) less than 1.04. In all cases, the isolated products of the coupling reaction showed a considerable increase in size as compared to the starting monodendron. For example, the **D-94** coupling product could be resolved by SEC from its starting monodendron **W-31-TMS**. To check for the possibility of partial coupling (eq 6), the SEC elution volumes of coupled products were compared against monodendrons of the same generation. Separation of these two species by SEC could be obtained only for the early members of the series. For the later generations, SEC showed no ability to resolve monodendrons and dendrimers of the same generation. For example, a 1:1 mixture of **D-46** and **W-31-TMS** coeluted to give a single, narrow peak that showed no evidence of a shoulder and gave a polydispersity of 1.03. Elemental compositions determined by combustion analyses are in agreement with their expected values for all of the tridendrons. Note, however, that the change in calculated composition from one generation to the next becomes even smaller for the dendrimers than for the corresponding monodendrons.

Initially, direct carbon dioxide Fourier transform laser desorption (LD-FTMS)[17] was used for mass spectrometry of the **D-4**, **D-10**, **D-22**, **D-46**, and **D-94** dendrimers. This procedure worked exceptionally well for the low-mass **D-4** and **D-10** samples, where mass measurement accuracy is better than 10 ppm and mass resolving power is 57 000 for **D-4** and 21 000 for **D-10**. However, direct LD-FTMS failed for the larger **D-22**, **D-46**, and **D-94** dendrimers, where it was necessary to use the technique of silver chemical ionization laser desorption to obtain spectra.[18] This procedure was effective for **D-22**, yielding well-resolved (22 000 resolving power) silver-attached molecular ion species and excellent mass measurement accuracy (Figure 5). However, **D-46** and **D-94** samples gave spectra with exceptionally poor mass resolution (<100) and worse mass accuracy than had been obtained for the first three members of the series.

Accordingly, the samples also were examined by time-of-flight ultraviolet matrix-assisted laser desorption/ionization (MALDI).[19,20] These measurements proved to be complementary to the LD-FTMS results, in that relatively poor mass measurement accuracy (errors between 0.05% and 0.31%) was obtained for the low-resolution **D-4**, **D-10**, and **D-22** molecular ions. However, higher resolving power (ca. 700) spectra were obtained with mass measurement errors of 95 ppm for the **D-46** and 27 ppm for **D-94** dendrimers (Figure 6). Interestingly, all of the MALDI time-of-flight spectra show evidence of dimers, and the **D-4**, **D-10**, and **D-22** spectra reveal the presence of trimeric species, as well.

The absence of focal point functionality, which provided a convenient NMR handle for the monodendrons, makes the analysis of the dendrimer spectra somewhat more difficult, especially for higher generations. For all of the members of the dendrimer species, ^1H NMR spectra show only a single *tert*-butyl singlet in the aliphatic region. The aromatic region shows several resonances and becomes more complicated and more

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(17) Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* **1985**, *57*, 520–524.

(18) Kahr, M. S.; Wilkins, C. L. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 453–460.

(19) Karas, M.; Bachmann, D.; Bahr, U.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Processes* **1987**, *78*, 53–68.

(20) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299–2301.

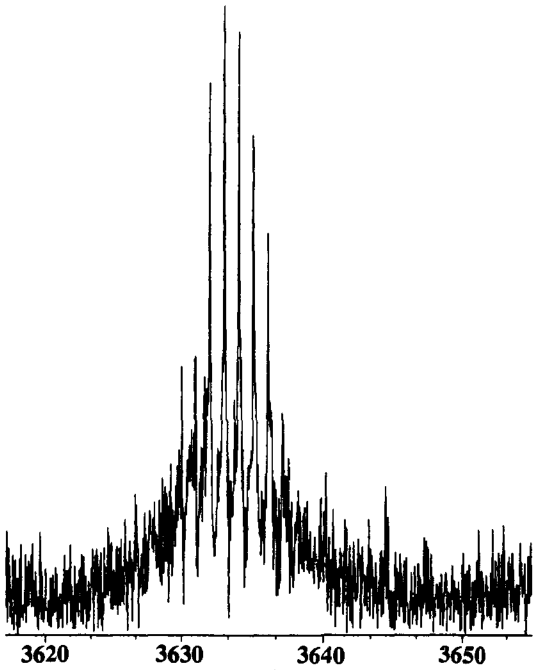

Figure 5. Partial LDCI Fourier transform mass spectrum of silver-attached dendrimer **D-22**, showing the molecular ion region with resolving power of 22 000 and average mass measurement accuracy for the isotopic multiplet of 14 ppm.

convoluted as the dendrimer size increases. The integral ratio of the *tert*-butyl protons to the total aromatic protons provides a rough estimate of the relative number of peripheral groups, although the value of this ratio rapidly becomes independent of generation as size increases.[21] Moreover, this ratio does not provide meaningful information about the quantity of possible impurities such as partial coupling products (eq 6) or diacetylene self-coupling side products.[16]

As in the case of monodendrons, benzene-d_6 can be used to obtain well-resolved ^{1}H NMR spectra for the aromatic region. Figure 7 shows a stacked plot of the aromatic regions of the ^{1}H NMR spectra of the series of tridendrons in benzene-d_6 at room temperature. For **D-4**, **D-10**, and **D-22**, sufficient chemical shift dispersion to allow complete assignment is readily achieved. In each case, an A_3 spin system plus a series of AX_2 spin systems can be clearly identified. For example, **D-4** shows a singlet and a doublet–triplet pair, **D-10** shows a singlet and two doublet–triplet pairs, and **D-22** shows a singlet and three doublet–triplet pairs. The relative integral of the singlet versus the doublet–triplet pairs follows the ratio required for the desired symmetrical tridendrons. All ^{13}C NMR resonances have been observed for **D-4, D-10, D-22**. For **D-46** and **D-94**, however, there exist overlaps in the one-dimensional ^{1}H and ^{13}C NMR spectra. Here again, variable-temperature ^{1}H NMR and two-dimensional NMR were helpful in elucidating the structures as described below.

Figure 8 shows the two-dimensional *J*-resolved ^{1}H NMR spectrum of the aromatic region of **D-46**. The overlapped portion in the one-dimensional ^{1}H NMR spectrum between δ 7.80 and 7.85 can clearly be seen to consist of a doublet, a singlet, a doublet, and a triplet. In addition to all the expected resonances, there are three sets of "extra" responses in the spectrum. Each set has eight responses. These "extra" responses arise due to strong coupling.[22,23] The lone A_3 spin system and the four AB_2 (almost AX_2) spin systems were easily identified from the COSY-45 spectrum.

Compared with **D-46**, the purification and NMR analysis of **D-94** proved to be more challenging. TLC of the 94-mer reaction mixture revealed the presence of two new products in addition to the 30-mer diacetylene byproduct carried over from the previous generation and a small amount of excess starting material. Separation of the reaction mixture was possible by careful silica gel chromatography in spite of rather severe band broadening. Size-exclusion chromatography of the two new products showed that they were nearly identical in size. The SEC elution profile in each case was a single sharp peak (M_w/M_n = 1.03) and corresponded to a molecular weight of 9.0×10^3 relative to narrow molecular weight polystyrene standards. This value is significantly larger than the value of 6.1×10^3 observed for the starting monodendron, which possesses 31 monomer units. The new product of higher R_f accounts for ca. 20% of the mixture and is identical (^{1}H NMR, TLC) to the 62-mer diacetylene synthesized independently. The major product (lower R_f) should thus correspond to the desired 94-mer, although the possibility that this substance is a 63-mer in which only two monodendrons coupled to triiodobenzene was examined. The major product gave an elemental composition by combustion analysis of that expected for **D-94**. This result disfavors the possibility that the 63-mer was isolated, since this monoiodide would have a carbon content 1% lower than the theoretical value of the desired tridendron.

Strong evidence in support of this conclusion has been obtained by extensive ^{1}H NMR experiments. In the aliphatic region, only a sharp singlet resonance corresponding to the *tert*-butyl protons is observed. The single *tert*-butyl resonance for all of the monodendrons and dendrimers reported here indicates that the peripheral groups interchange rapidly on the NMR time scale. As in the cases of monodendrons, NMR solvent and temperature have been optimized to attain adequate chemical shift dispersion in the aromatic region of the spectrum for complete assignment. Good chemical shift dispersion is realized in benzene-d_6 or THF-d_8. Spectra recorded in $CDCl_3$, again, are very congested and contain little useful information. The ^{1}H NMR chemical shifts in the aromatic region of **D-94** showed strong variation with temperature. This made it possible to run spectra under conditions in which it was possible to resolve all aromatic resonances (e.g., 300 K for **D-94**). Five triplet–doublet pairs corresponding to five different AB_2 (nearly AX_2) spin systems and a singlet can be identified. Integral ratios made it possible to assign each triplet–doublet pair to a tier of **D-94**. The relative integral intensity of these spin systems follows the predicted ratio of 1:2:4:8:16. Most importantly, a small singlet is observed at δ 7.68, confirming the presence of a C_3 rotational axis in this molecule. This singlet displays a fairly strong temperature-dependent chemical shift such that it moves downfield at higher temperatures. At 300 K, it is possible to adequately separate the singlet from the intense doublet at δ 7.66 and obtain accurate integral intensities. Careful integration of the singlet against the furthest downfield doublet gives the expected 1:2 ratio. Two-dimensional ^{1}H NMR experiments helped to further confirm the structure. The COSY-45 spectrum of the 94-mer tridendron in benzene-d_6 at 295 K showed five cross peaks corresponding to the five different spin systems expected for this compound. Two-dimensional *J*-resolved spectroscopy established that each of these cross peaks correlates a triplet–doublet pair.

Other explanations that are consistent with the synthetic chemistry have also been considered to account for the appearance of the δ 7.68 singlet resonance. However, the evidence presented below suggests that the singlet is indeed due to protons on the core ring of **D-94**. First, the T_1 value of protons giving rise to the δ 7.68 resonance is similar to those on neighboring aromatic

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[21] The calculated ratio, *R*, of *tert*-butyl to total aromatic protons as a function of generation, *n*, for the tridendrons is given by,

$$R = \frac{18(2^n)}{3(2^{n+1}) - 2} \qquad \text{(iii)}$$

For generations 0, 1, 2, and 3, the value of R = 4.5, 3.6, 3.27, and 3.13, respectively. As $n \rightarrow \infty$, R approaches a limiting value of 3.0.

[22] Kumar, A. *J. Magn. Reson.* **1978**, *30*, 227.

[23] Bodenhausen, G.; Freeman, R.; Morris, G. A.; Turner, D. L. *J. Magn. Reson.* **1978**, *31*, 75.

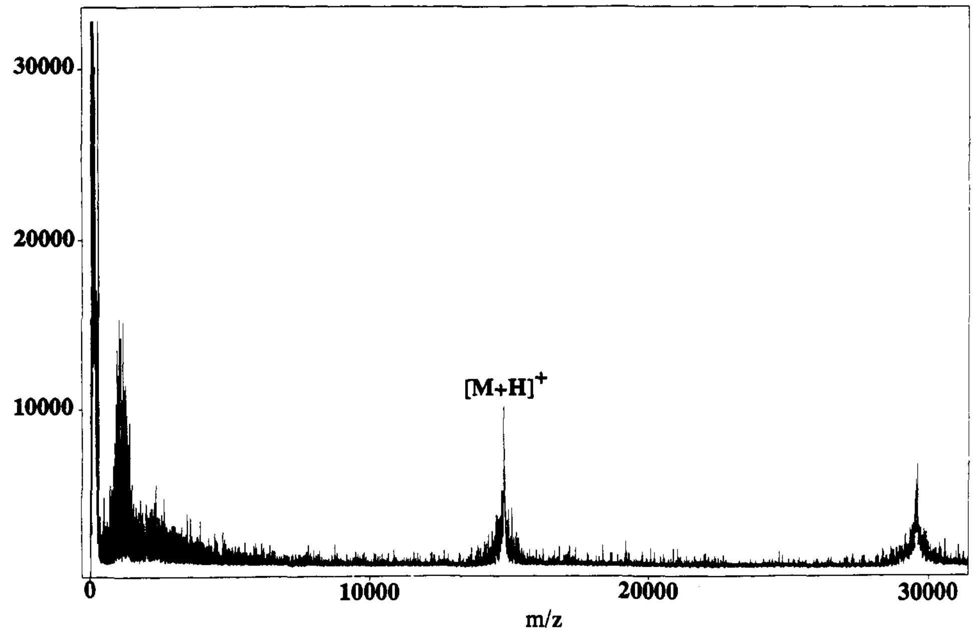
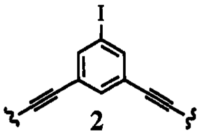


Figure 6. MALDI-TOF spectrum of dendrimer **D-94** showing $[M + H]^+$ ion with *m/z* 14 776.2.

rings (ca. 4 s). Second, by comparison to the ^{1}H NMR spectrum of authentic 62-mer diacetylene, the possibility of this side product can be ruled out. Third, if only two monodendrons coupled to triiodobenzene, then the innermost ring should have structure **2** or, if reductive deiodination occurred, then structure **3** is possible.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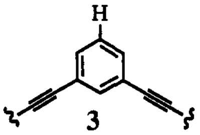
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Resonances due to protons on **2** or **3** would show the appearance of a singlet only if these spin systems were strongly second order. Given the expected chemical shifts of **2** and **3**, this is not likely. Moreover, integration of the δ 7.68 singlet resonance with respect to the furthermost downfield doublet would be 3:4 and 4:4 for **2** and **3**, respectively, instead of the observed 1:2 ratio. Therefore, these possibilities were ruled out.

To confirm that the singlet in the ^{1}H NMR of **D-94** indeed comes from the core, the labeled dendrimer **D-94-*d*$_3$** was prepared using 1,3,5-triiodo-2,4,6-trideuteriobenzene as the core. The chemical structure of this labeled compound is shown in Figure 4. Figure 9 compares ^{1}H NMR spectra of the aromatic region of **D-94-*d*$_3$** and **D-94** at two different temperatures. Note that at the higher temperature (330 K), the **D-94** singlet is downfield of the δ 7.70 triplet, while at the lower temperature (305 K) the **D-94** singlet is upfield of the δ 7.70 triplet. The spectra of the isotope-labeled dendrimer **D-94-*d*$_3$** are identical with the spectra of **D-94** except for the absence of the singlet. We conclude that this resonance corresponds to the A_3 spin system of the dendrimer's core. The complete assignment of the ^{1}H NMR spectrum together with the correct element analysis and mass spectrometry results confirms the chemical structure of **D-94**. This dendrimer has the molecular formula $C_{1134}H_{1146}$ and a molecular weight of 14 776. It represents one of the largest, pure synthetic hydrocarbons hitherto known.[24]

Having completed the synthesis of this compact series of stiff dendrimers up to **D-94**, it is of interest to consider the possibility of preparing higher generations. What are the limiting factors governing the synthesis and the size of these dendritic molecules? From the above results, it seems that one of the limiting factors is the formation of a diacetylene byproduct. Although this side product can be detected in low levels (<2%) in small molecule cross-coupling reactions, this reaction pathway becomes significant for the higher generation dendrimers. Efforts to prevent this oxidative dimerization by rigorous exclusion of oxygen have not yielded improved results. The reason for the change in reaction pathway is not known at this time. Factors such as steric inhibition may become important. Steric inhibition is the term used[4b] to describe the diminished reactivity experienced by functional groups at the focal point of monodendrons, and it has been observed in other dendritic systems. This limitation points to the need for new synthetic schemes to realize the synthesis of higher generations of dendritic polymers.[24] Another limiting factor is the ability to purify and characterize these structure-controlled macromolecules. The effort required for rigorous characterization becomes extreme as the size of the dendrimer increases. Finally, solubility is obviously an important factor. A small change in the peripheral group functionality (i.e., 4-*tert*-butylphenyl to 3,5-di-*tert*-butylphenyl) provides a rather dramatic improvement in solubility of the tridendrons. In particular, tridendrons having 4-*tert*-butylphenyl peripheral groups are poorly soluble, while those having 3,5-di-*tert*-butylphenyl groups are soluble in pentane at room temperature. This result is quite surprising given the high aromatic content and stiffness of these macromolecules. Qualitatively, we note that the solubility as a function of molecular size for the di-*tert*-butylphenyl series is lowest for mono- and tridendrons having 10–15 monomer units, and solubility *improves* as the molecular size grows beyond this range. Powder X-ray diffraction shows that those dendrimers having only 10–15 monomers are at least partly crystalline, while the higher members are totally amorphous.

Double-Stage Convergent Method. Scheme 4 shows our attempt to prepare a fourth-generation phenylacetylene dendrimer using the double-stage convergent method. Note that the final product, **D-106**, contains 12 additional phenylacetylene units compared to the corresponding fourth-generation dendrimer (**D-94**). The additional units in **D-106** are para-linked aromatics introduced during the synthesis of hypercore **C-22-[I]$_{12}$**. The synthesis of this core begins by coupling 2 equiv of **M-3-[N$_3$Et$_2$]$_2$** with monomer **1** to give **M-7-[N$_3$Et$_2$]$_4$** in 86% yield after the trimethylsilyl groups are removed. Three equivalents of **M-7-[N$_3$Et$_2$]$_4$** were then coupled with tribromobenzene, giving the fully souble and completely characterized dodecatriazene **C-22-[N$_3$Et$_2$]$_{12}$**. Transformation to the corresponding aryl iodide gave hypercore **C-22-[I]$_{12}$**, which was largely insoluble in common organic solvents. However, in

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[24] We have recently reported the preparation of even larger hydrocarbon dendrimers using a growth scheme in which the monomer size changes as a function of generation: Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354.

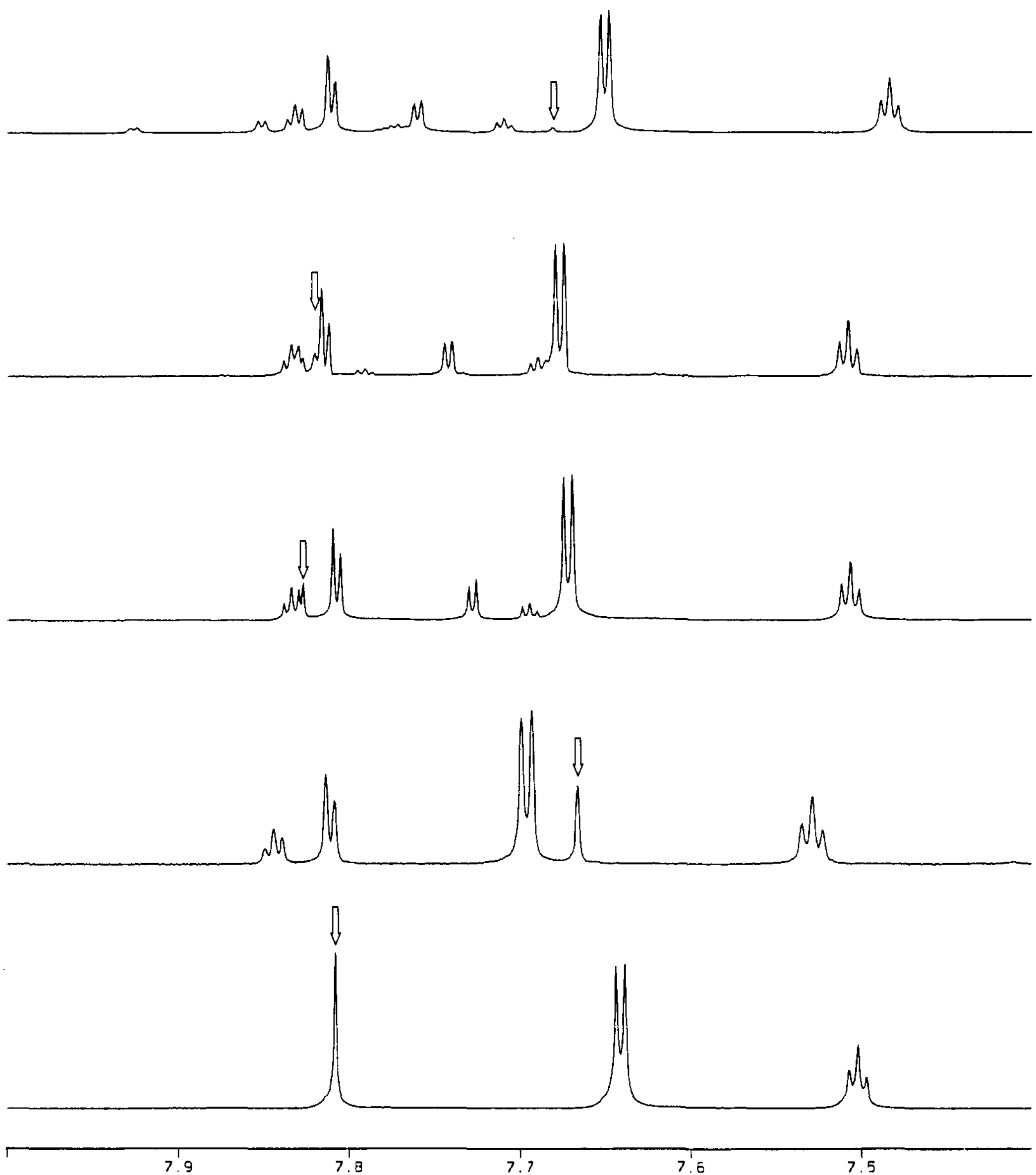

Figure 7. Stacked plot of the aromatic regions of the ^1H NMR spectra of **D-4** (bottom), **D-10**, **D-22**, **D-46**, and **D-94** (top) in benzene-d_6 (295 K, 360 MHz). The arrows show the positions of the core singlet resonances.

contrast to the hexaiodo core **C-10-[I]$_6$** (Scheme 2), **C-22-[I]$_{12}$** was slightly soluble in boiling chlorobenzene and gave satisfactory elemental analysis. The poor solubility of this compound prevented its NMR characterization, but a single narrow peak was observed by SEC and a single spot by TLC.

A suspension of **C-22-[I]$_{12}$** in chlorobenzene/triethylamine was reacted with 15 equiv of monodendron **W-7-H** at 70 °C in the presence of a palladium catalyst. During this time, the suspended core was observed to disappear, and a new product was observed by TLC. SEC showed this new product to be of significantly higher molecular weight than either **W-7-H** or the core **C-22-[I]$_{12}$** (see Table 1). The product was soluble in a wide range of organic products and easily isolated from the small amount of diacetylene byproduct and unreacted monodendron by silica gel chromatography. The yield of the presumed **D-106** was only 36% based on core **C-22-[I]$_2$**. The SEC trace of this product gave a single, sharp, and symmetrical peak with no indication of contamination and a M_w/M_n of 1.03. Elemental analysis showed no indication of remaining iodide and a carbon–hydrogen composition that is essentially consistent with $C_{1230}H_{1194}$ expected for **D-106** (Table 2). Proton NMR of the coupling product in benzene-d_6 showed only a single *tert*-butyl resonance and a complex set of resonances in the aromatic region. Although the pattern was similar to that of **D-94**, we were unable to obtain sufficient resolution to make a complete assignment. The protons residing on the para-linked aromatic ring could clearly be identified as a broad singlet (second order) around δ 7.40. Careful examination of the region where ortho-iodo protons are expected showed no indication of remaining iodide. This evidence supports the structure of **D-106**, although the possibility of dendrimers with one or more branches missing cannot unambiguously be ruled out.

Experimental Section

General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Dry triethylamine was obtained by vacuum transfer from calcium hydride. Dry THF and benzene were obtained by vacuum transfer from sodium and benzophenone. Methyl iodide was vacuum transferred from molecular sieves. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-360 or AM-300 in the indicated solvents at the indicated fields; chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The ^1H NMR assignments for the tridendrons are reported using the following lettering scheme: core protons are labeled H_a, and the remaining aromatic protons are labeled by proceeding sequentially outward from the core to the periphery. For quantitative NMR, a relaxation delay time was used such that the time

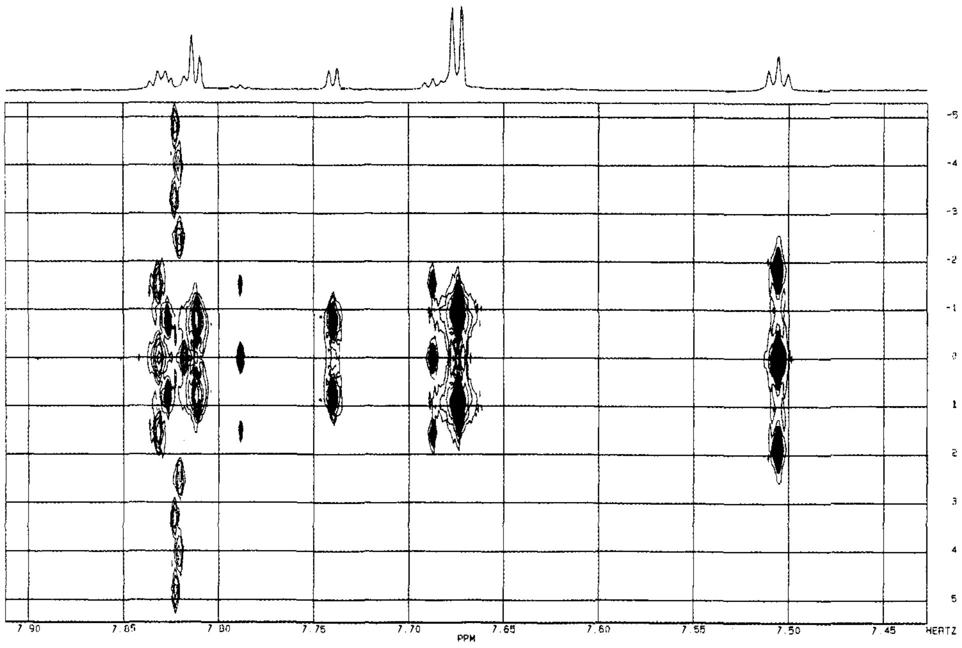

Figure 8. Two-dimensional, *J*-resolved ^{1}H NMR spectrum of the aromatic region of **D-46** in benzene-d_6 (295-K, 360 MHz).

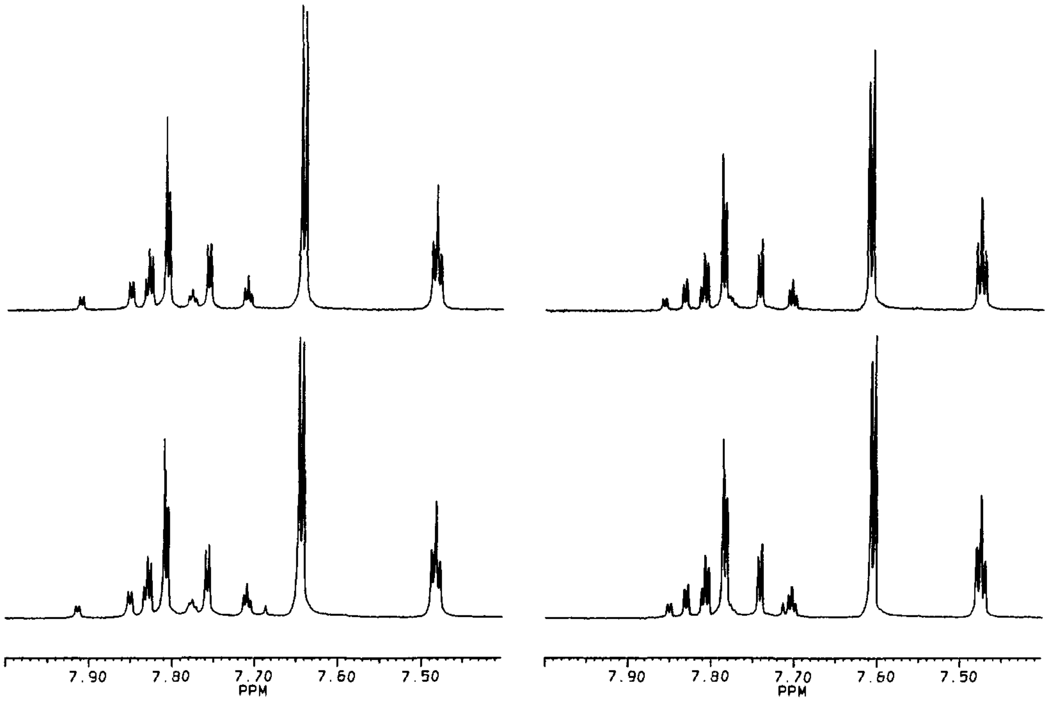

Figure 9. Comparison of ^{1}H NMR spectra in the aromatic region of **D-94** (bottom spectra) and **D-94-d_3** (top spectra) at 305 K (spectra in left column) and 330 K (spectra in right column).

between 45° pulses corresponded to $3T_1$. Analytical thin liquid chromatography was performed on kieselgel F-254 precoated TLC plates. Silica for flash chromatography was silica gel 60 (230–400 mesh) from EM Science. Gas chromatography (GC) was performed on an HP-5890 Series II gas chromatograph equipped with a 25-m × 0.2-mm × 0.33-mm HP-1 silicone column. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Size-exclusion chromatography (SEC) was performed using a Waters 6000A solvent delivery system and Model 440 absorptance detector at 254 nm. A series of three Microstyragel columns of pore sizes 500, 10^3, and 10^4 Å were used and were calibrated with narrow molecular weight polystyrene standards. SEC data were obtained in THF at 23 °C. Cascade nomenclature follows the procedure reported by Newkome et al.[25]

Laser Desorption Mass Spectrometry. (i) Sample Preparation. For infrared laser desorption Fourier transform mass spectrometry (LD-FTMS), all dendrimer samples were prepared by dissolving ca. 1 mg of sample in methylene chloride, followed by deposition upon stainless steel probe tips by the aerosol spray technique described previously.[18] Dendrimer **D-4** and **D-10** samples were deposited directly onto a stainless steel probe tip. The **D-22** sample was prepared by spraying 50 μL of a saturated silver nitrate ethanol solution (containing ca. 3 mg of silver nitrate) onto the rotating probe tip prior to dendrimer deposition. Samples were introduced into the vacuum system, and the source cell pressure was reduced to 2.2×10^{-8} Torr and the analyzer cell pressure to 2.0×10^{-9} Torr before analysis.

For ultraviolet matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) of the **D-46** and **D-94** dendrimers, *trans*-retinoic acid was dissolved in methylene chloride (Fisher, ACS grade) to form a 0.03 M solution, which was combined with methylene chloride solutions of the dendrimers to produce solutions with a matrix-to-analyte ratio of 550. Prior to use, the retinoic acid matrix solution was irradiated with fluorescent light for approximately 48 h at

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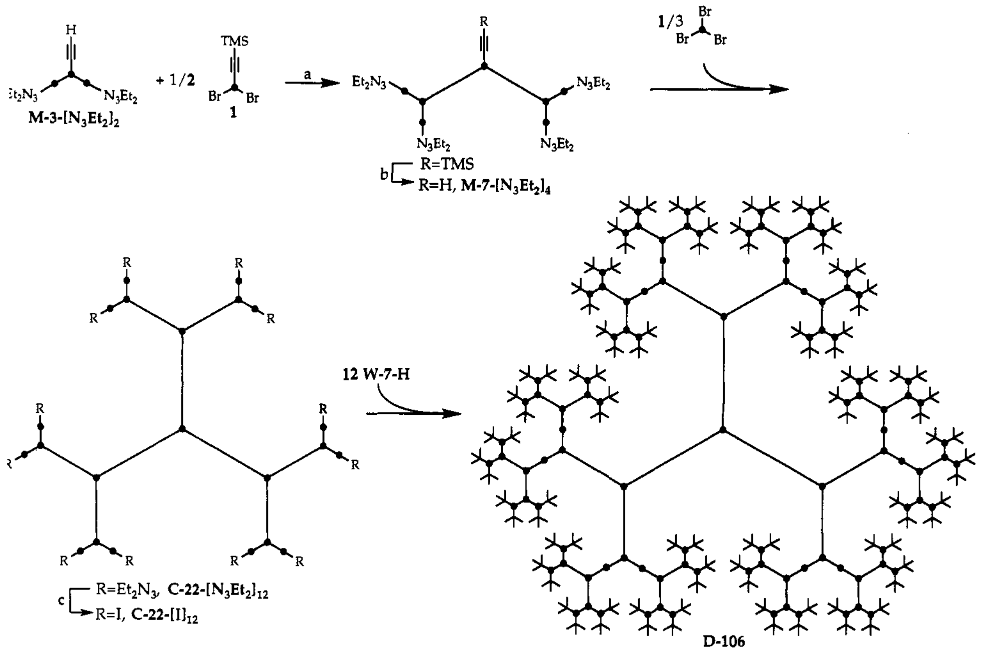
(25) Newkome, G. R.; Baker, G. R.; Young, J. K.; Traynham, J. G. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 641–51.

Scheme 4. Preparation of Tridendron **D-106** by the Double-Stage Convergent Method[a]



[a] (a) $[Pd(dba)_2]/PPh_3/CuI/TEA/80$ °C. (b) $KOH/MeOH/CH_2Cl_2$. (c) $CH_3I/100$ °C.

room temperature. For **D-46** dendrimer analysis, an aliquot corresponding to 75 pm of the **D-46** sample was transferred to the surface of a stainless steel sample pin and allowed to dry. Following that, a 0.02 M solution of poly(ethylene glycol)-1000 in methylene chloride was aerosol sprayed onto the pin to form a film on top of the dried **D-46**/matrix mixture. For **D-94** dendrimer analysis, a 0.9-μL aliquot of the PEG-1000 solution was deposited upon a sample pin and allowed to dry, prior to addition of an aliquot of the **D-94**/matrix mixture corresponding to 74 picomoles of **D-94**.

Instrumentation. (a) Fourier Transform Mass Spectrometry. Fourier transform mass spectrometry (FTMS) was performed using a FTMS-2000 Fourier transform mass spectrometer (Millipore-Extrel FTMS, Madison, WI) equipped with a 7-T superconducting magnet, differentially pumped source and analyzer regions separated by a 2-mm conductance limit, and an automatic solids probe. The FTMS was interfaced to a Tachisto 215 pulsed CO_2 laser for desorption. The CO_2 laser beam was directed into the mass spectrometer through a ZnSe window in the source flange and focused to ~1-mm^2 spot size on the tip of the solids probe by an off-axis paraboloid mirror mounted on the source cell assembly. The laser delivers approximately 10^6–10^8 W/cm^2 per 80 ± 40-ns pulse.

D-4 and **D-10** spectra were obtained by transferring the laser-desorbed ions from the source cell to the analyzer using 200- (**D-4**) and 700-μs (**D-10**) transfer times and a 0.2-V analyzer cell trapping voltage. Following ion transfer and a 1-s delay, ions were excited using chirp excitation from 2 to 200 kHz at a rate of 240 Hz/μs for the **D-4** compound and 180 Hz/μs for the **D-10**. **D-4** spectra were obtained at 200-kHz bandwidth, collecting 262 144 data points, and **D-10** spectra were obtained at 100-kHz bandwidth, acquiring 131 072 data points.

Spectra of **D-22** were obtained using only the source cell. Following laser desorption, after a 5-s delay chirp, excitation was performed from 2 to 200 kHz at 180 Hz/μs, with a data acquisition bandwidth of 30 kHz to obtain 131 072 data points.

Data were base-line-corrected followed by augmentation with an equal number of zeros before Fourier transformation. For FTMS mass assignments, all spectra were postcalibrated with poly(ethylene glycol)-1000 spectra obtained within 1 h under trapping conditions identical to those used for the dendrimers. Mass assignments were determined using a Lorentzian fit to the data points of the spectrum (not interpolated).

(b) Time-of-Flight Mass Spectrometry. Ultraviolet MALDI time-of-flight mass spectra were measured with a LaserTec Research mass spectrometer (Vestec Corporation, Houston, TX) equipped with a Nd-YAG Laser (Lumonics YAGMASTER 200, Lumonics Ltd., Warwickeshire, England). All samples were desorbed with the frequency-tripled (355 nm) output of the laser. The sample irradiance was controlled with a variable attenuator (Model 935-5-OPT UV, Newport Research Corp.) and focused to illuminate an average spot size of diameter 20 μm.

All spectra were measured in the linear time-of-flight mode (1.2-m flight path). Ions were accelerated with a potential of 29 kV and detected by an ion multiplier biased at 5 kV, except for **D-10** dendrimer spectra, where the multiplier was held at 3.5 kV. The resulting ion current was monitored at 2-ns intervals with a digital oscilloscope (Model TDS 520, Tektronix Inc.). Mass spectra were generated from the average of 7–23 single acquisitions, and the resulting spectra were filtered with a 5-point Savitsky-Golay smooth.

Mass assignments were prepared by estimating the centroid of the peaks with a commercial software package (Grams 386). Dendrimer mass spectra for **D-46** and **D-94** were internally calibrated using sodium-attached ions of PEG 1000.

Starting Materials. The following compounds were prepared according to literature methods: 1,3,5-triiodobenzene (**1**),[26] 4-*tert*-butylphenylacetylene,[27] 4-methoxyphenylacetylene,[28] 1-4′-ethynylphenyl-3,3-diethyltriazene,[29] (trimethylsilyl)acetylene.[30]

General Procedure for Synthesis of Monodendrons (W-*x*-TMS) and Tridendrons (D-*x*). A heavy-walled flask was charged with terminal acetylene (1.1 equiv per halide), aryl iodide or bromide (1.0 equiv), $Pd(dba)_2$ (0.02 equiv), triphenylphosphine (0.10 equiv), copper(I) iodide (0.02 equiv), and dry triethylamine. For **D-106**, chlorobenzene was used as a cosolvent because of the poor solubility of reactants. The concentrations of the reaction varied from 0.3 to 0.05 M depending on the solubility of reactants and the scale of the reaction. The flask was then evacuated and back-filled with argon 3 times, capped, and stirred at 60 °C for 12 h or longer. The disappearance of terminal acetylene was checked by TLC. When the reaction was complete, the mixture was diluted with dichloromethane, washed with water (3×), dried over anhydrous magnesium sulfate, and filtered. Following concentration, the product was purified as outlined below.

General Procedure for Deprotection of Monodendrons (W-*x*-TMS). The monodendron (W-*x*-TMS, 1.0 equiv) was dissolved in dichloromethane, and absolute methanol was added dropwise to the point of saturation. Excess solid potassium hydroxide was added, and the suspension was stirred under argon at room temperature for about 30 min. After complete deprotection (checked by TLC or GC), water was added, and the aqueous layer was extracted with dichloromethane (3×). The combined organic extracts were dried over anhydrous magnesium

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[26] (a) Bellamy, F. D. *Tetrahedron Lett.* **1984**, *25*, 839. (b) Shepherd, R. G. *J. Org. Chem.* **1947**, *12*, 275. (c) An improved procedure for preparing 1,3,5-triiodobenzene has been reported by Wuest and co-workers: Wang, X.; Wuest, J. D., unpublished results. We thank Professor Wuest for providing this information.

[27] This compound is prepared from 4-*tert*-butyl-1-bromobenzene and (trimethylsilyl)acetylene according to the general palladium-catalyzed coupling procedure.

[28] This is prepared from 4-iodoanisole and (trimethylsilyl)acetylene according to the general palladium-catalyzed coupling procedure.

[29] Wu, Z.; Moore, J. S., unpublished results.

[30] Purchased from Aldrich Chemical Co. or from Lancaster Synthesis.

sulfate and evaporated to dryness. The resulting **W-*x*-H** was pure enough to use without further purification.

3′,5′-Di-*tert*-butyl-2-phenyl-1-(trimethylsilyl)acetylene (W-1-TMS). 3,5-Di-*tert*-butylphenyl(trifluoromethane)sulfonate (37.6 g, 0.111 mol) and (trimethylsilyl)acetylene (16.4 g, 0.167 mol) were reacted at 60 °C for 48 h following the general coupling procedure. The concentrated crude product was passed through 150 g of silica gel eluted with hexane, and the resulting material was recrystallized from cold pentane (19.4 g, 61%): mp 147–148 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 2H), 7.34 (s, 1H), 1.33 (s, 18H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 150.67, 126.22, 122.97, 122.04, 106.43, 92.45, 34.77, 31.32, 0.11. Anal. Calcd for $C_{19}H_{30}Si$: C, 79.64; H, 10.55. Found: C, 79.54; H, 10.26.

W-3-TMS (2-Cascade:(2-(trimethylsilyl)ethynyl)benzene[2-3,5]:5-ethynyl-1,3-di-*tert*-butylbenzene). Monomer **1** and **W-1-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with pentane increasing to 25:1 hexane/CH_2Cl_2 to give **W-3-TMS** as a colorless foam: yield 93%; ^{1}H NMR ($CDCl_3$) δ 7.73–7.78 (m, 1H), 7.67–7.69 (m, 2H), 7.44–7.52 (m, 6H), 1.42 (s, 36H), 0.35 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 150.90, 134.22, 134.17, 125.95, 124.21, 123.84, 123.04, 121.88, 103.52, 95.45, 91.69, 86.65, 34.04, 31.36, –0.07; HRMS calcd for $C_{43}H_{54}Si$ 598.3995, found 598.3992. Anal. Calcd for $C_{43}H_{54}Si$: C, 86.22; H, 9.09. Found: C, 86.02; H, 9.21.

W-7-TMS (4-Cascade:(2-(trimethylsilyl)ethynyl)benzene[2-3,5]:5-ethynyl-1,3-phenylene:5-ethynyl-1,3-di-*tert*-butylbenzene). Monomer **1** and **W-3-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 25:1 hexane/CH_2Cl_2 increasing to 15:1 hexane/CH_2Cl_2 to give **W-7-TMS** as a colorless powder: yield 80%; ^{1}H NMR ($CDCl_3$) δ 7.69–7.82 (m, 9H), 7.48–7.51 (m, 12H), 1.42 (s, 72H), 0.35 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.01, 134.78, 134.47, 134.33, 133.91, 126.01, 124.54, 124.22, 123.75, 123.51, 123.13, 121.91, 103.21, 96.13, 91.99, 89.29, 88.66, 86.64, 34.84, 31.37, –0.12; HRMS calcd for $C_{91}H_{102}Si$ 1222.7751, found 1222.7748. Anal. Calcd for $C_{91}H_{102}Si$: C, 89.30; H, 8.40. Found: C, 89.18; H, 8.32.

W-15-TMS (8-Cascade:(2-(trimethylsilyl)ethynyl)benzene[2-3,5]:(5-ethynyl-1,3-phenylene)^2:5-ethynyl-1,3-di-*tert*-butylbenzene). Monomer **1** and **W-7-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 12:1 hexane/CH_2Cl_2 increasing to 10:1 hexane/CH_2Cl_2 to give **W-15-TMS** as a colorless powder: yield 51%; ^{1}H NMR ($CDCl_3$) δ 7.66–7.74 (m, 21H), 7.41–7.44 (M, 24H), 1.35 (s, 144H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 150.95, 135.05, 134.58, 134.50, 134.40, 134.14, 133.94, 125.99, 124.41, 124.14, 123.89, 123.71, 123.52, 123.36, 123.14, 121.75, 103.02, 96.18, 91.85, 89.40, 88.94, 88.84, 88.51, 86.58, 34.85, 31.34, –0.14. Anal. Calcd for $C_{187}H_{198}Si$: C, 90.79; H, 8.07. Found: C, 90.61; H, 8.17.

W-31-TMS (16-Cascade:(2-(trimethylsilyl)ethynyl)benzene[2-3,5]:(5-ethynyl-1,3-phenylene)^3:5-ethynyl-1,3-di-*tert*-butylbenzene). Monomer **1** and **W-15**-H were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 10:1 hexane/CH_2Cl_2 increasing to 6:1 hexane/CH_2Cl_2 to give **W-31-TMS** as a colorless powder: yield 21%; ^{1}H NMR (360 MHz, benzene-d_6) δ 7.83 (t, J = 1.6 Hz, 8H), 7.80 (d, J = 1.6 Hz, 16H), 7.79 (t, J = 1.6 Hz, 2H), 7.75 (d, J = 1.6 Hz, 4H), 7.74 (d, J = 1.6 Hz, 2H), 7.73 (d, J = 1.5 Hz, 8H), 7.70 (t, J = 1.6 Hz, 1H), 7.69 (t, J = 1.5 Hz, 4H), 7.67 (d, J = 1.8 Hz, 32H), 7.51 (t, J = 1.8 Hz, 16H), 1.24 (s, 288H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 150.94, 134.50, 134.38, 133.93, 125.97, 124.40, 123.90, 123.77, 123.66, 123.51, 123.34, 123.13, 121.75, 91.84, 89.42, 89.01, 88.98, 88.82, 88.73, 88.50, 86.58, 34.83, 31.33, –0.16. Anal. Calcd for $C_{379}H_{390}Si$: C, 91.53; H, 7.90. Found: C, 91.28; H, 8.12.

Attempted Synthesis of W-63-TMS. A one-neck flask with a side arm was charged with **W-31-H** (119 mg, 0.024 mmol), **1** (3.1 mg, 0.009 mmol), bis(dibenzylideneacetone)palladium(0) (1.6 mg, 0.003 mmol), triphenylphosphine (6 mg, 0.023 mmol), copper(I) iodide (0.6 mg, 0.003 mmol), and dry triethylamine (3 mL). The flask was then capped, degassed, back-filled with nitrogen, and stirred at 70 °C for 72 h. The disappearance of terminal acetylene was checked by TLC. After completion, the reaction mixture was diluted with dichloromethane, washed with water (3×), dried over anhydrous magnesium sulfate, and filtered. Following concentration, the major product was purified by flash column chromatography, eluting with 7:1 hexane/CH_2Cl_2 increasing to 6:1 hexane/CH_2Cl_2 to give a offwhite powder. ^{1}H NMR spectrum (benzene-d_6, 360 MHz) showed that the isolated compound contained no $(CH_3)_3Si$- proton resonances between 0.2 and 0.5 ppm. The strong *tert*-butyl proton resonance and the aromatic proton resonances are consistent with the structure of the oxidative dimerization product of the starting monodendron **W-31**-H. Elemental analysis also supports this conclusion. Anal. Calcd for the oxidative dimer $C_{752}H_{762}$: C, 92.16; H, 7.84. Found: C, 91.86; H, 7.83.

D-4 (3-Cascade:benzene[3-1,3,5]:5-ethynyl-1,3-di-*tert*-butylbenzene). Tribromobenzene and **W-1-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with pentane increasing to hexane to give **D-4** as a white powder: yield 77%; mp 229–231 °C; ^{1}H NMR (benzene-d_6) δ 7.81 (s, 3H, H_a), 7.663 (d, J = 1.8 Hz, 6H, H_b), 7.518 (t, J = 1.8 Hz, 3H, H_c), 1.25 (s, 54H, *tert*-butyl H); ^{13}C NMR ($CDCl_3$) δ 150.94, 133.87, 125.97, 124.26, 123.06, 121.91, 91.61, 86.80, 34.83, 31.35. Anal. Calcd for $C_{54}H_{66}$: C, 90.31; H, 9.69. Found: C, 90.30; H, 9.67.

D-10 (6-Cascade:benzene[3-1,3,5]:5-ethynyl-1,3-phenylene:5-ethynyl-1,3-di-*tert*-butylbenzene). Tribromobenzene and **W-3-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 20:1 hexane/CH_2Cl_2 increasing to 10:1 hexane/CH_2Cl_2 to give **D-10** as a white powder: yield 73%; ^{1}H NMR (benzene-d_6) δ 7.845 (t, J = 1.4 Hz, 3H, H_c), 7.812 (d, J = 1.4 Hz, 6H, H_b), 7.698 (d, J = 1.8 Hz, 12H, H_d), 7.665 (s, 3H, H_a), 7.53 (t, J = 1.8 Hz, 6H, H_e), 1.25 (s, 108H, *tert*-butyl H); ^{13}C NMR ($CDCl_3$) δ 151.00, 134.52, 134.47, 133.98, 126.02, 124.45, 123.90, 123.42, 123.17, 121.81, 91.88, 89.38, 88.59, 86.62, 34.85, 31.35. Anal. Calcd for $C_{126}H_{138}$: C, 91.58; H, 8.42. Found: C, 91.61; H, 8.90.

D-22 (12-Cascade:benzene[3-1,3,5]:(5-ethynyl-1,3-phenylene)^2:5-ethynyl-1,3-di-*tert*-butylbenzene). Triiodobenzene and **W-7-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 10:1 hexane/CH_2Cl_2 increasing to 7:1 hexane/CH_2Cl_2 to give **D-22** as a white powder: yield 84%; ^{1}H NMR (360 MHz, benzene-d_6) δ 7.83 (t, J = 1.6 Hz, 6H, H_e), 7.82 (s, 3H, H_a), 7.80 (d, J = 1.6 Hz, 12H, H_d), 7.72 (d, J = 1.5 Hz, 6H, H_b), 7.69 (t, J = 1.5 Hz, 3H, H_c), 7.67 (d, J = 1.8 Hz, 24H, H_f), 7.50 (t, J = 1.8 Hz, 12H, H_g), 1.25 (s, 216H, *tert*-butyl H); ^{13}C NMR ($CDCl_3$) δ 151.10, 134.74, 134.61, 134.51, 134.03, 126.16, 126.07, 124.59, 124.07, 123.95, 123.83, 123.49, 123.22, 121.92, 92.01, 89.55, 89.12, 88.92, 88.60, 86.68, 34.89, 31.38. Anal. Calcd for $C_{270}H_{282}$: C, 91.94; H, 8.06. Found: C, 91.69; H, 8.09.

D-46 (24-Cascade:benzene[3-1,3,5]:(5-ethynyl-1,3-phenylene)^3:5-ethynyl-1,3-di-*tert*-butylbenzene). Triiodobenzene and **W-15-H** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 8:1 hexane/CH_2Cl_2 increasing to 6:1 hexane/CH_2Cl_2 to give **D-46** as a white powder: yield 54%; ^{1}H NMR (360 MHz, benzene-d_6) δ 7.82–7.84 (m, 18H, H_g and H_b), 7.82 (s, 3H, H_a), 7.81 (d, J = 1.5 Hz, 24H, H_f), 7.79 (t, J = 1.5 Hz, 3H, H_c), 7.74 (d, J = 1.5 Hz, 12H, H_d), 7.69 (t, 6H, J = 1.5 Hz, H_e), 7.67 (d, J = 1.8 Hz, 48H, H_h), 7.51 (t, J = 1.8 Hz, 24H, H_i), 1.24 (s, 432H, *tert*-butyl H); ^{13}C NMR ($CDCl_3$) δ 150.95, 134.71, 134.49, 134.38, 133.91, 125.96, 124.46, 123.95, 123.84, 123.70, 123.38, 123.11, 121.81, 91.91, 89.46, 89.09, 88.84, 88.52, 86.59, 34.81, 31.31. Anal. Calcd for $C_{558}H_{570}$: C, 92.10; H, 7.90. Found: C, 91.92; H, 8.09.

D-94 (48-Cascade:benzene[3-1,3,5]:(5-ethynyl-1,3-phenylene)^4:5-ethynyl-1,3-di-*tert*-butylbenzene). A heavy-walled flask with a side arm was charged with **W-31-H** (140 mg, 0.0286 mmol), triiodobenzene (3.3 mg, 0.007 mmol), bis(dibenzylideneacetone)palladium(0) (1.6 mg, 0.003 mmol), triphenylphosphine (6 mg, 0.023 mmol), copper(I) iodide (0.6 mg, 0.003 mmol), and dry triethylamine (3 mL). The flask was then capped, degassed, back-filled with nitrogen, and stirred at 40 °C for 2 days. The disappearance of terminal acetylene was checked by TLC. After completion of the reaction, the mixture was diluted with dichloromethane, washed with water (3×), dried over anhydrous magnesium sulfate, and filtered. TLC (5:1 hexane/CH_2CL_2) of the final reaction mixture revealed the presence of two new products (R_f = 0.37 and 0.32) in addition to the 30-mer diacetylene byproduct (R_f = 0.66) carried over from the previous generation and a small amount of excess starting material (R_f = 0.52). Separation of this mixture was possible by careful silica gel column chromatography using a gravity column, eluting with 7:1 hexane/CH_2Cl_2 increasing to 6:1 hexane/CH_2Cl_2. The new product of higher R_f (R_f = 0.37) accounts for ca. 20% of the mixture and is identical (^{1}H NMR, TLC) to the 62-mer diacetylene synthesized independently (see attempted synthesis of **W-63-TMS** described earlier). **D-94** is obtained as a off-white glass (40 mg): yield 37%; ^{1}H NMR (360 MHz, benzene-d_6) δ 7.94 (d, J = 1.6 Hz, 6H, H_b), 7.86 (d, J = 1.6 Hz, 12H, H_d), 7.84 (t, J = 1.5 Hz, 24H, H_i), 7.81 (d, J = 1.5 Hz, 48H, H_h), 7.79 (t, J = 1.5 Hz, 3H, H_c), 7.77 (t, J = 1.5 Hz, 6H, H_e), 7.76 (d, J = 1.5 Hz, 24H, H_f), 7.71 (t, J = 1.5 Hz, 12H, H_g), 7.68 (s, 3H, H_a), 7.66 (d, J = 1.8 Hz, 96H, H_j), 7.49 (t, J = 1.8 Hz, 48H, H_k), 1.37 (s, 864H, *tert*-butyl H); ^{13}C NMR (360 MHz, $CDCl_3$) δ 150.86, 134.69, 134.45, 134.32, 134.06, 133.88, 133.32, 125.95, 124.69, 124.36, 123.84, 123.73, 123.64, 123.34, 123.05, 121.77, 91.84, 89.41, 89.08, 88.87, 88.54, 86.61, 34.78, 31.29. Anal. Calcd for $C_{1134}H_{1146}$: C, 92.18; H, 7.82. Found: C, 91.96; H, 7.75.

D-106 (48-Cascade:benzene[3-1,3,5]:(5-ethynyl-1,3-phenylene)^2:(*p*-5-ethynyl-1,3-phenylene:5-ethynyl-1,3-phenylene:5-ethynyl-1,3-di-*tert*-butylbenzene. A heavy-walled flask with a side arm was charged with **W-7-H** (32 mg, 0.028 mmol), **C-22-[I]$_{12}$** (5.7 mg, 0.0015 mmol), bis(dibenzylideneacetone)palladium(0) (3 mg, 0.005 mmol), triphenylphosphine (7 mg, 0.027 mmol), copper(I) iodide (1.5 mg, 0.008 mmol), dry triethylamine (2 mL), and chlorobenzene (1 mL). The flask was then capped, degassed, back-filled with nitrogen, and stirred at 40 °C for 72 h. The disappearance of terminal acetylene was checked by TLC. After completion of the reaction, the mixture was diluted with dichloromethane, washed with water (3×), dried over anhydrous magnesium sulfate, and filtered. Following concentration, the product was purified by flash column chromatography, eluting with 5:1 hexane/CH$_2$Cl$_2$ increasing to 3:1 hexane/CH$_2$Cl$_2$ to give **D-106** as a white powder (9 mg):yield 36%; ^{1}H NMR (CDCl$_3$) δ 7.36–7.82 (m, 330H), 1.33 (s, 864H); ^{13}C NMR (CDCl$_3$) δ 150.93, 133.91, 132.39, 131.73, 130.91, 128.83, 125.97, 124.17, 123.14, 121.73, 96.13, 91.82, 86.67, 86.60, 34.83, 31.33. Anal. Calcd for $C_{1230}H_{1194}$: C, 92.47; H, 7.53. Found: C, 92.14; H, 7.90.

M-3-[N$_3$Et$_2$]$_2$. Monomer **1** (1.0 equiv) and 1-4′-ethynylphenyl-3,3-diethyltriazene (2.2 equiv) were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 4:1 hexane/CH$_2$Cl$_2$ increasing to 3:2 hexane/CH$_2$Cl$_2$ to give a yellowish oil: yield 69%; ^{1}H NMR (CDCl$_3$) δ 7.63–7.64 (m, 1H), 7.58–7.59 (m, 2H), 7.49–7.51 (d, 4H, J = 7 Hz), 7.41–7.44 (d, 4H, J = 7 Hz), 3.75–3.81 (q, 8H), 1.26–1.30 (t, 12H), 0.28 (s, 9H); ^{13}C NMR (CDCl$_3$) δ 151.28, 133.96, 133.94, 132.35, 124.21, 123.71, 120.42, 118.84, 103.50, 95.37, 91.16, 87.60, 40.97, 12.02, –0.15. Anal. Calcd for $C_{35}H_{40}N_6Si$: C, 73.39; H, 7.04; N, 14.67. Found: C, 73.39; H, 6.99; N, 14.58. The trimethylsilyl group was removed according to the general procedure to give **M-3-[N$_3$Et$_2$]$_2$**.

M-7-[N$_3$Et$_2$]$_4$. Monomer **1** (1.0 equiv) and **M-3-[N$_3$Et$_2$]$_2$** (2.4 equiv) were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 1:1 hexane/CH$_2$Cl$_2$ increasing to 1:2 hexane/CH$_2$Cl$_2$ to give a yellowish oil: yield 86%; ^{1}H NMR (CDCl$_3$) δ 7.62–7.67 (m, 9H), 7.50–7.53 (d, 9H, J = 9 Hz), 7.41–7.44 (d, 9H, J = 9 Hz), 3.75–3.82 (q, 16H), 1.26–1.31 (t, 24H), 0.29 (s, 9H); ^{13}C NMR (CDCl$_3$) δ 151.61, 134.89, 134.42, 134.37, 133.82, 132.54, 124.77, 124.37, 123.93, 123.64, 122.66, 119.23, 103.39, 96.17, 91.59, 89.43, 88.72, 87.56, 45.00, 12.86, –0.12. Anal. Calcd for $C_{75}H_{74}N_{12}Si$: C, 76.89; H, 6.37; N, 14.35. Found: C, 76.65; H, 6.29; N, 14.46. The trimethylsilyl group was removed according to the general procedure to give **M-7-[N$_3$Et$_2$]$_4$**.

General Procedure for the Synthesis of Iodo-Terminated Cores C-*x*-[I]$_y$. A heavy-walled glass tube joined to a Teflon screw valve was charged with the triazene precursor **C-*x*-[N$_3$Et$_2$]$_y$** and was taken up in freshly distilled iodomethane (ca. 0.1 M in precursor). The solution was degassed and placed under a nitrogen head space, and the tube was sealed. After the mixture was heated for 12 h at 110 °C, the starting triazene had completely reacted. During this time, salt precipitated from the solution. The workup procedure depended on the solubility of the final product as outlined below.

C-10-[N$_3$Et$_2$]$_6$. 1,3,5-Tribromobenzene and **M-3-[N$_3$Et$_2$]$_2$** were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 1:1 hexane/CH$_2$Cl$_2$ increasing to 1:3 hexane/CH$_2$Cl$_2$ to give **C-10-[N$_3$Et$_2$]$_6$** as a yellowish oil: yield 76%; ^{1}H NMR (CDCl$_3$) δ 7.68 (s, 3H), 7.62–7.68 (m, 9H), 7.49–7.52 (d, 12H, J = 8 Hz), 7.41–7.44 (d, 12H, J = 8 Hz), 3.76–3.83 (q, 24H), 1.27–1.32 (t, 36H); ^{13}C NMR (CDCl$_3$) δ 151.66, 135.02, 134.49, 132.56, 124.91, 122.59, 120.66, 119.09, 91.84, 87.51, 80.72, 74.79, 12.92. Anal. Calcd for $C_{102}H_{96}N_{18}$: C, 77.83; H, 6.15; N, 16.02. Found: C, 77.53; H, 6.18; N, 16.05.

Attempted Preparation of C-10-[I]$_6$. Hexatriene **C-10-[N$_3$Et$_2$]$_6$** was reacted with iodomethane according to the general procedure for triazene deprotection. After completion of the reaction, the mixture was washed with dichloromethane, and the undissolved solid was purified by solid liquid extraction with dichloromethane using a Soxhlet extractor: yield 75%. Anal. Calcd for $C_{78}H_{36}I_6$: C, 54.01; H, 2.09. Found: C, 52.77; H, 2.09.

C-22-[N$_3$Et$_2$]$_{12}$. 1,3,5-Tribromobenzene and **W-7-[N$_3$Et$_2$]$_4$** were reacted using the general coupling procdure, and the product was purified by flash chromatography, eluting with 1:10 hexane/CH$_2$Cl$_2$ increasing to pure CH$_2$Cl$_2$ to give **C-22-[N$_3$Et$_2$]$_{12}$** as a yellowish oil: yield 70%; ^{1}H NMR (CDCl$_3$) δ 7.62–7.67 (m, 30H), 7.49–7.52 (d, 24H, J = 8 Hz), 7.43–7.47 (d, 24H, J = 8 Hz), 3.76–3.83 (q, 48H), 1.26–1.31 (t, 72H); ^{13}C NMR (CDCl$_3$) δ 151.56, 135.18, 134.42, 133.79, 132.50, 124.76, 124.27, 123.43, 122.80, 120.63, 119.13, 91.64, 89.88, 88.37, 87.71, 80.52, 75.13, 45.30, 12.88. Anal. Calcd for $C_{222}H_{198}N_{36}$: C, 79.12; H, 5.92; N, 14.96. Found: C, 79.14; H, 5.86; N, 14.99.

C-22-[I]$_{12}$. Dodecatriazene **C-22-[N$_3$Et$_2$]$_{12}$** was reacted with iodomethane according to the general procedure for triazene deprotection. After completion, the reaction mixture was washed with dichloromethane, and the undissolved solid was purified by extraction with dichloromethane under a Soxhlet condenser: yield 61%. Anal. Calcd for $C_{174}H_{78}I_{12}$: C, 56.62; H, 2.02. Found: C, 56.47; H, 2.19.

1,3,5-Triiodo-2,4,6-Trideuteriobenzene. Proton deuterium exchange of 1,3,5-triiodobenzene was accomplished with trifluoromethanesulfonic acid-d_1. Triiodobenzene (110 mg, 0.24 mmol) was treated with trifluoromethanesulfonic acid-d_1 (3 mL) at 120 °C for 72 h. The crude product was checked by GCMS and purified by recrystallization from methanol. The final product was >90% deuterated by GCMS.

Acknowledgment is made to the National Science Foundation for support through Grant DMR-9212054. J.S.M. also thanks the NSF Young Investigator Program, Grant CHE-9257050 (1992–1997), and the 3M company for support through their awards program for untenured faculty. C.L.W. gratefully acknowledges support from the National Science Foundation under Grant CHE-92-01277 and from a grant by the W. M. Keck Foundation.

Supplementary Material Available: Stacked plot of the aromatic region of ^{1}H NMR spectra of **W-31-TMS** in benzene-d_6 as a function of temperature; stacked plot of the aromatic region of the ^{1}H NMR spectra of **D-94** in benzene-d_6 as a function of temperature; two-dimensional COSY-45 ^{1}H NMR spectrum of the aromatic region of **D-94** (295 K, 360 MHz); ^{1}H NMR spectrum of **D-94** showing integrated intensities; ^{1}H NMR spectrum of the oxidative dimerization product of **W-31-H** showing integrated intensities; ^{1}H NMR spectrum of **W-31-H** showing integrated intensities; elemental analysis data for phenylacetylene mono- and tridendrons (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.