Dendrimers

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Pushing the Synthetic Limit: Polyphenylene Dendrimers with "Exploded" Branching Units—22-nm-Diameter, Monodisperse, Stiff Macromolecules[**]

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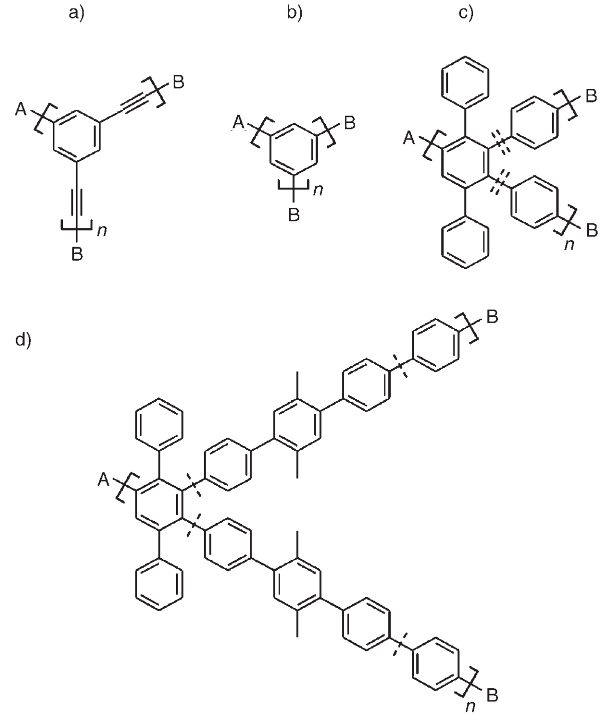
The majority of effort in dendrimer chemistry has been devoted to constructions with flexible branching units, thereby introducing a variety of conformational aspects into the molecule, such as the nature of the molecular density and the location and orientation of the chain ends.[1] Rigidification of the dendrimer, and in some cases, control over the chain-end locations, has come from a variety of approaches,[2] including the use of stiff building blocks such as that of poly(1-3,5-phenylene ethynylene),[3] poly(1-3,5-phenylene),[4] and polyphenylene dendrimers based on pentaphenylbenzene[5] (Scheme 1 a, b, and c, respectively). Beyond a critical generation, the convergent synthesis of dendrimers necessitates the use of flexible building blocks or smaller dendrons.[6] To circumvent this limitation, a gradient of branching unit lengths has been employed[7] in the case of a dendrimer with 1-3,5-phenylene ethynylene branching points, thus installing greater volume at the interior of the molecule. A similar size-modulation approach to the branching unit is herein proposed for the enlargement of the parent, polyphenylene dendrimers. Linear enlargement of the arms of the general dendritic repeat unit (Scheme 1 d) should directly translate into increased dendrimer radii without requiring a larger core moiety (Figure 1). The synthesis of polyphenylene dendrimers around a tetraphenylmethane core has thus far been limited to the fourth generation[8] because of incomplete conversion at higher generations, presumably the prohibitive result of steric crowding at the chain ends.[9] In light of this observation, a terphenyl spacer was introduced into each arm of the branching unit to decrease the congestion of the chain ends at higher generations (Figure 1). Since the connectivity of the branching points in the dendrimers with extended arms



Scheme 1. Stiff, dendritic AB$_2$ repeat units: a) poly(1-3,5-phenylene ethynylene), b) poly(1-3,5-phenylene), c) poly(4′-4,4″-(3′,6′-diphenyl *o*-terphenylene)), and d) "exploded" polyphenylene by the extension of each arm by insertion of a linear terphenyl between each set of dashed lines of the general polyphenylene repeat unit shown in (c).

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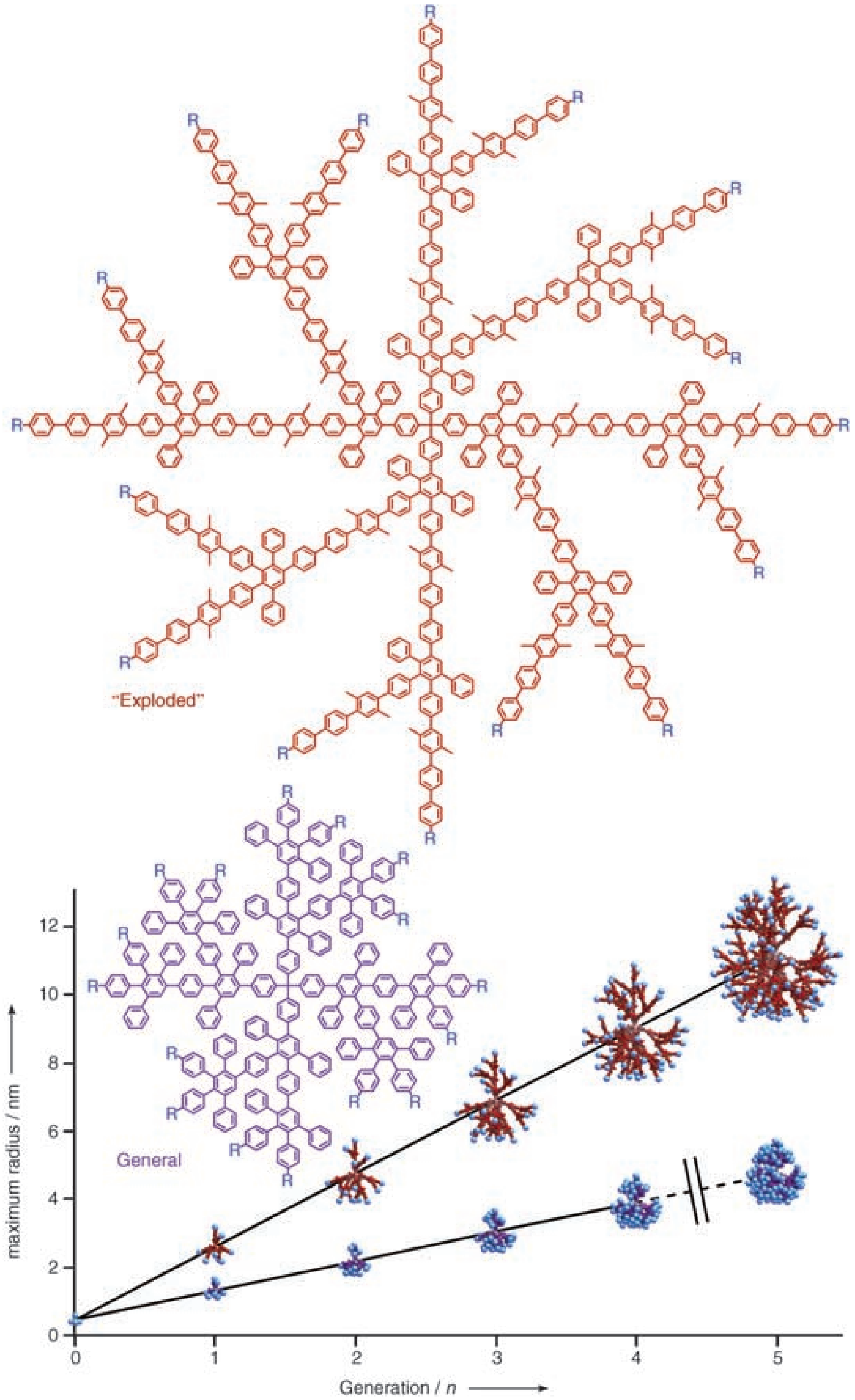
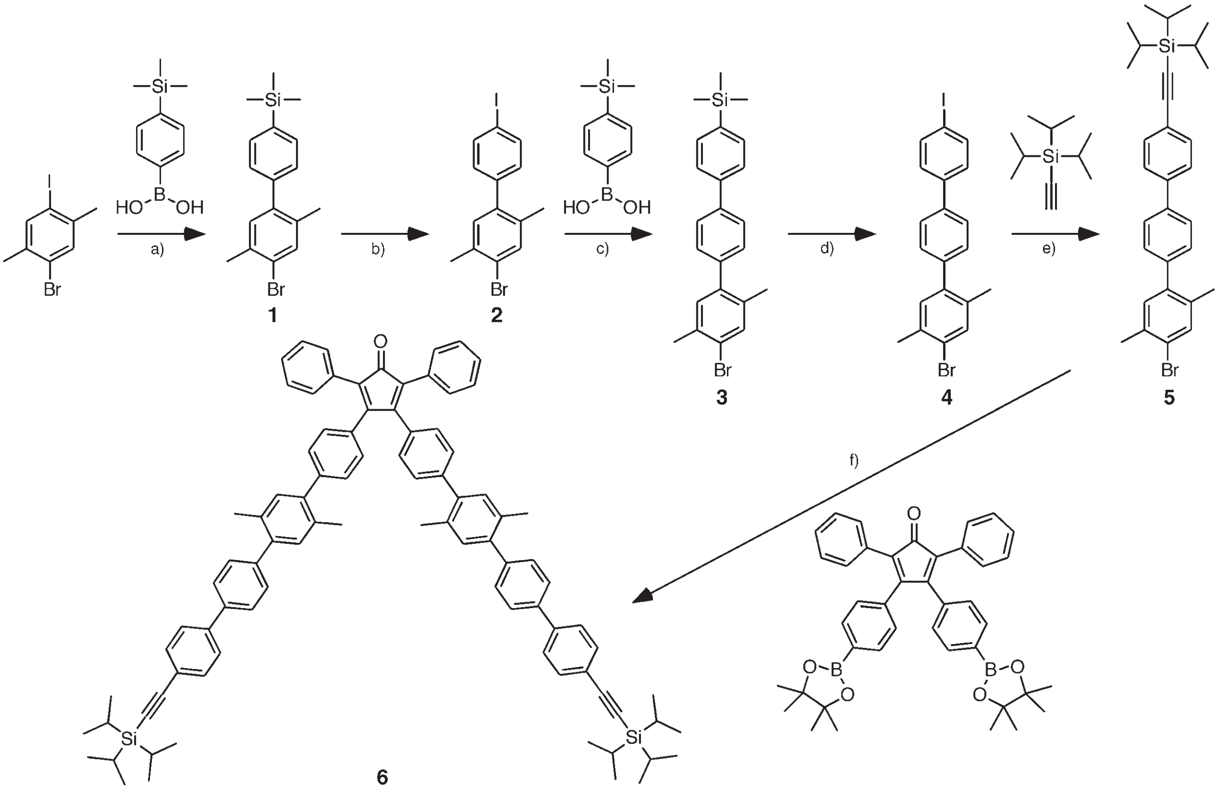


Figure 1. Scaling of the dendrimer radii for general polyphenylene dendrimers and new "exploded" polyphenylene dendrimers with identical branching-point connectivity but increased branching unit arm length through the use of a 2′,5′-dimethyl-*p*-terphenyl spacer. Second-generation dendrimers for each type are illustrated in greater detail. The iterative illustrations were generated using POV-Ray and are qualitatively similar to the results of MMFF94 molecular mechanics calculations for generations 1–4. The maximum radius was determined by the length of the longest linear oligophenylene arm for each generation.

is the same as for the parent polyphenylene dendrimers, the radii should be 150 % greater than the comparable radii of the parent cases. This situation would enable the stepwise synthesis of a structurally perfect particle with a diameter greater than 20 nm, which well exceeds the dimension of the narrowly disperse but not monodisperse particles that have been synthesized by self-assembly or multiphase approaches.[10]

The key component in the dendrimer synthesis is the masked AB_2 building block 3,4-bis-(2′,5′-dimethyl-4‴-triisopropylsilylethynyl-1,1′:4′,1″:4″,1‴-quaterphenyl-4-yl)-2,5-diphenylcyclopentadienone (**6**; Scheme 2) which bears an active tetraphenylcyclopentadienone and two terminal aryl acetylenes, or Diels–Alder dienophiles, protected with bulky triisopropylsilyl (T*i*PS) groups. While the solubilities of the final dendrimers were not anticipated to be poor, the solubilities of the *p*-terphenyl intermediates were expected to complicate the synthesis. As such, two methyl groups were introduced as side chains from the beginning by using 1-bromo-4-iodo-2,5-dimethylbenzene. An efficient, iterative, selective Suzuki coupling[11] (Scheme 2) using the more-reactive aryl iodide, compared to the aryl bromide, with commercially available 4-trimethylsilylphenylboronic acid was performed to give 4-bromo-2,5-dimethyl-4′-trimethylsilylbiphenyl (**1**). Removal of the trimethylsilyl group with ICl[12] provided 4-bromo-4′-iodo-2,5-dimethylbiphenyl (**2**). The cycle was repeated to obtain 4-bromo-4″-iodo-2,5-dimethyl-1,1′:4′,1″-terphenyl (**4**). The aryl iodide was treated with trimethylsilylacetylene under Sonogashira/Hagihara conditions[13] to afford **5**. The final step was the twofold Suzuki coupling of the remaining aryl bromide with 3,4-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,5-diphenylcyclopentadienone to furnish **6**.[14] Chromatographic purification was performed for all steps.

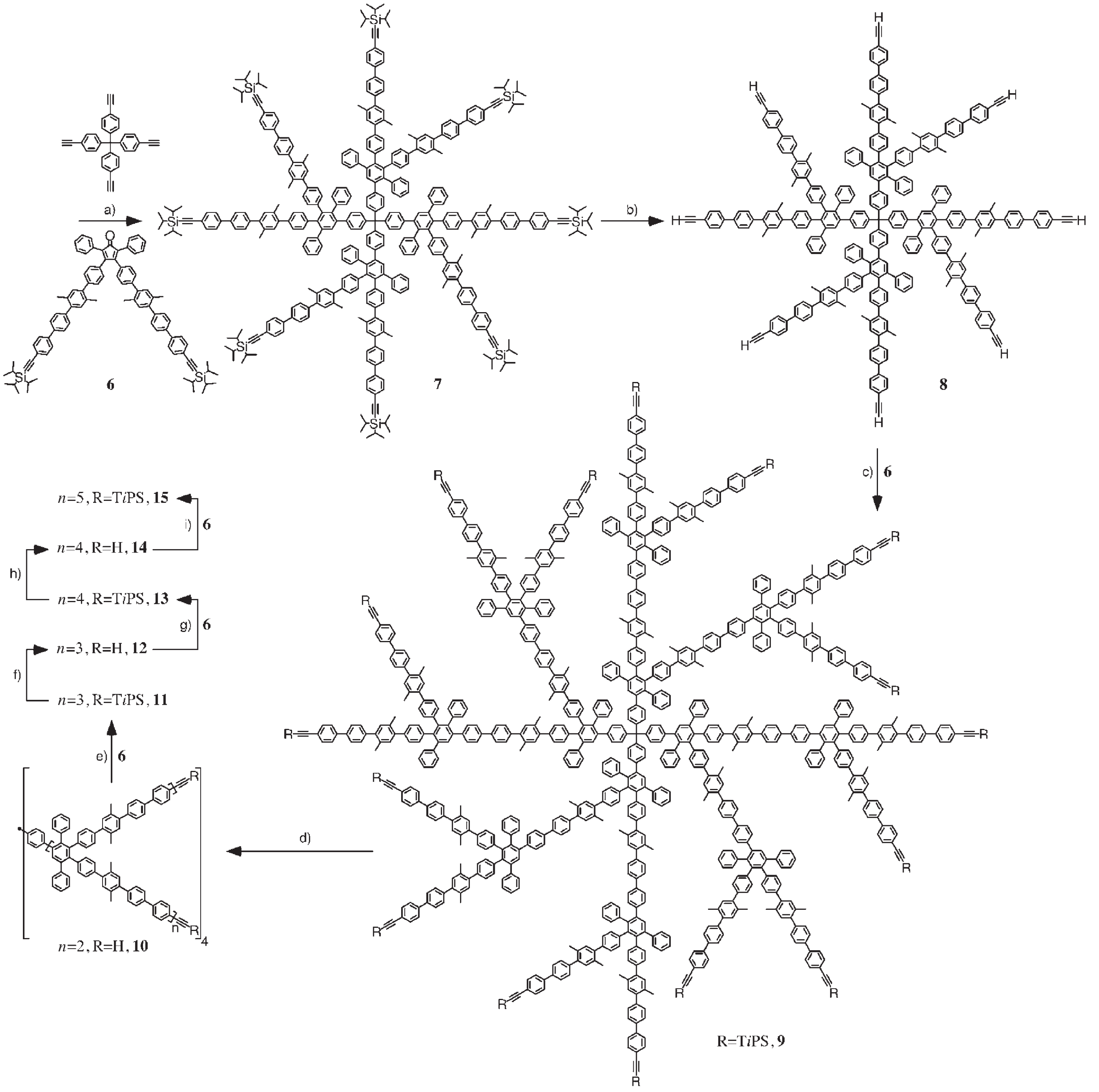
The strategy for the synthesis of the new dendrimers with extended arms (Scheme 3) was directly analogous to the synthesis of the parent polyphenylene dendrimers. Fourfold Diels–Alder reactions of the masked AB_2 building block **6** with tetra(4-ethynylphenyl)methane[8] produced the first-generation dendrimer **7** bearing eight T*i*PS chain end groups. Removal of excess **6** was accomplished by chromatographic purification. Removal of the T*i*PS groups with tetrabutylammonium fluoride trihydrate gave the first-generation dendrimer **8** with eight terminal ethynyl units



Scheme 2. Synthesis of the masked, AB_2 building block **6**: a) K_2CO_3, $[Pd(PPh_3)_4]$, toluene, water, reflux, 62%; b) ICl, CCl_4, CH_2Cl_2, 0°C, 96%; c) K_2CO_3, $[Pd(PPh_3)_4]$, toluene, water, ethanol, reflux, 83%; d) ICl, CH_2Cl_2, 0°C, 87%; e) $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, NEt_3, CH_2Cl_2, 80%; f) K_2CO_3, $[Pd(PPh_3)_4]$, toluene, water, ethanol, reflux, 48%.

quantitatively. After quenching the reaction with water and precipitation in methanol, **8** was ready for subsequent generational growth. The cycle was repeated through to the fourth generation, and a final coupling yielded the fifth-generation dendrimer with 128 T*i*PS chain ends. Removal of excess **6** from the reaction mixture was achieved, beginning with the synthesis of the second-generation dendrimer **9**, by first adsorbing the dendrimer onto silica gel. The adsorbate was washed with acetone until the purple color of the eluent disappeared, and then the dendrimer was extracted with THF and reprecipitated in acetone. Synthetic details for all compounds presented here are included in the Supporting Information.

^{1}H NMR spectroscopic analysis (see Supporting Information) is consistent with the growth of each new generation of dendrimer (**7**, **9**, **11**, **13**, and **15**). The aromatic resonances for the third-, fourth-, and fifth-generation dendrimers (**11**, **13**, and **15**, respectively) were virtually identical, as the resonances from the tetraphenylmethane core were diluted. Resonances for the four inequivalent methyl groups (two closely spaced near $\delta = 2.3$ ppm and two others further separated at $\delta = 2.13$ and 2.10 ppm for **7**) of the repeat unit were nearly unchanged upon deprotection and growth to the next generations, as they are too far from sites of reactivity. Integration of the T*i*PS chain end resonances, relative to both the aromatic backbone resonances and the methyl side-chain resonances, is in agreement with complete conversion into the dendrimer product. Size-exclusion chromatography (SEC) results (THF; Figure 2) showed a progressive decrease in the elution volume for each subsequent generation (**7**, **9**, **11**, **13**, and **15**), while the decrease in the elution volume was smaller going to the fifth-generation dendrimer **15**;[15] the peak shape confirmed that **15** is smaller than the exclusion limit of the columns. A high-molecular-weight shoulder was present, which gave rise to a broader polydispersity than the earlier generation dendrimers. The shoulder, presumed to be the result of aggregation, has been observed for large generation dendrimers[2c] and was further broadened at higher concentration. Neither ^{1}H NMR spectroscopy nor SEC, however, has the inherent dynamic range to determine whether the final coupling reactions go exclusively to completion (for example, whether the pure dendrimer or a mixture of the dendrimer and nearly complete conversions is produced). MALDI-TOF analysis (using dithranol as matrix, and in some cases, a suitable cationization agent was added) was relied upon to detect the presence of the final dendrimers. The Diels–Alder reactions were stopped when the product molecular ion was the only large molecular ion observed (Table 1). The molecular ions of the desired dendrimeric products were detected for the first three generations, **7**, **9**, and **11**. At higher generation (**13**, Figure 3) an ion corresponding to MALDI fragmentation at the core could be observed (calcd: m/z 16370, found: m/z 16339) in addition to the molecular ion (calcd: m/z 65494, found: m/z 65430). This fragmentation mechanism, removal of one dendron from the core, has been typically observed with polyphenylene den-



Scheme 3. Synthesis of the first- through to fifth-generation "exploded" polyphenylene dendrimers with a tetraphenylmethane core: a, c, e, g, i) *o*-xylene, reflux; b, d, f, h) tetrabutylammonium fluoride trihydrate, THF, RT; a) 85 %, b) 76 %, c) 96 %, d) 75 %, e) 87 %, f) 75 %, g) 64 %, h) 58 %, i) 65 %.

drimers bearing a tetraphenylmethane core.[16] No ions could be observed in the MALDI-TOF spectrum of the fifth-generation dendrimer **15** using dithranol as matrix; however, the MALDI-TOF spectrum obtained using DCTB[17] as matrix (Figure 4) and sufficient laser power to observe any ions showed a weak signal for the molecular ion (calcd: m/z 134162, found: m/z 135290). Further proof of the existence of **15** came from the detected ions, which resulted from a large degree of fragmentation and coalescence of the highly reactive fragments with the molecular species. In addition to fragmentation at the core (m/z 33948, 67980, 101273), an additional fragmentation pathway was identified at the first branching point away from the core (m/z 16975, 50971, 84626, 118281, and higher coalescence ions). Increasing the relative amount of matrix or the introduction of cationization agents did not improve the intensity of the molecular ion. The fragmentation is possibly a result of the spectral overlap between the nitrogen laser (337 nm) used for excitation of the matrix and the UV absorbance for the higher generation dendrimers ($\lambda_{max} = 300$ nm). The fourth-generation dendrimer **13** appears to be the limit for efficient generation and detection of the molecular ion without substantial

Table 1: Summary and comparison of the size characteristics for new polyphenylene dendrimers **7**, **9**, **11**, **13**, and **15** compared with hydrogen end-capped general polyphenylene dendrimers **A**, **B**, and **C**.[8,16] [a]

Compound	Molecular formula	Aryl rings	Chain ends	Molecular mass [g mol^{-1}]	MALDI-TOF MS [g mol^{-1}]	SEC M$_p$(PS)[b] [g mol^{-1}]	SEC PDI	Theo. radius[c] [nm]	DLS radius[d] [nm]	TEM radius[e] [nm]	Dendrimer density[f] [g mL^{-1}]
"exploded" dendrimers											
C(Ph([G1](C≡C-T*i*PS)$_2$)$_4$ (**7**)	$C_{393}H_{388}Si_8$	48	8	5336	5443 (Ag)	8000	1.04	2.5	2.0	–	0.26
C(Ph([G2](C≡C-T*i*PS)$_4$)$_4$ (**9**)	$C_{1041}H_{964}Si_{16}$	136	16	13 924	13 935 (K)	22 000	1.05	4.2	3.6	–	0.12
C(Ph([G3](C≡C-T*i*PS)$_8$)$_4$ (**11**)	$C_{2337}H_{2116}Si_{32}$	312	32	31 101	31 168	38 900	1.03	6.9	5.2	–	0.09
C(Ph([G4](C≡C-T*i*PS)$_{16}$)$_4$ (**13**)	$C_{4929}H_{4420}Si_{64}$	664	64	65 454	65 430 (K)	83 200	1.05	9.0	9.0	–	0.04
C(Ph([G5](C≡C-T*i*PS)$_{32}$)$_4$ (**15**)	$C_{10113}H_{9028}Si_{128}$	1368	128	134 162	135 290	114 200	1.10	11.0	11.8	11	0.03
general dendrimers											
C(Ph([G2](H)$_4$)$_4$ (**A**)	$C_{385}H_{260}$	64	16	4886	4916 (K)	3900	1.04	1.8	1.5	–	0.57
C(Ph([G3](H)$_8$)$_4$ (**B**)	$C_{865}H_{580}$	144	32	10 974	11 113 (Ag)	7900	1.03	2.5	2.2	2.6	0.41
C(Ph([G4](H)$_{16}$)$_4$ (**C**)	$C_{1825}H_{1220}$	304	64	23 150	23 194 (K)	13 800	1.05	3.2	2.9	3.0	0.38

[a] All MALDI-TOF mass spectra were acquired by irradiating the 1:250 analyte/matrix mixture with a nitrogen laser (337 nm) using dithranol as matrix and optional cationization agent, a trifluoroacetate salt, if specified, except for that of **15** which was acquired using DCTB.[17] [b] SEC was performed at room temperature in THF using SEC columns with 500, 10^4, and 10^6 Å porosities and calibrated against narrowly disperse, linear polystyrene (PS) standards. [c] Theoretical radii were determined using MMFF94 molecular mechanics calculations, by evaluating the distance between the central carbon atom and the chain end of the longest linear oligophenylene arm. [d] DLS experiments were performed using a krypton ion laser (647.1 nm), a toluene filled index matching bath, and detected at 60, 90, 120, and 150° with respect to the incident beam and were measured in THF for **7**, **9**, **11**, **13**, and **15** and in toluene for **A**, **B**, and **C**.[8,16] The hydrodynamic radii were calculated using the Stokes–Einstein equation. [e] TEM samples were prepared by spin-coating 10^{-8}–10^{-9} M CH_2Cl_2 solutions onto mica substrates and subsequently shadowed with a tungsten/tantalum alloy at high vacuum, followed by deposition of a thin carbon support. The films were floated off the mica substrates onto a water surface and transferred to 600-mesh hexagonal copper grids for imaging. [f] The dendrimer densities were calculating by dividing the molecular mass by the hydrodynamic volume determined from DLS studies, and are substantially lower for the new polyphenylene dendrimer series, which suggests much higher porosities for the same series than those of the general polyphenylene dendrimers.

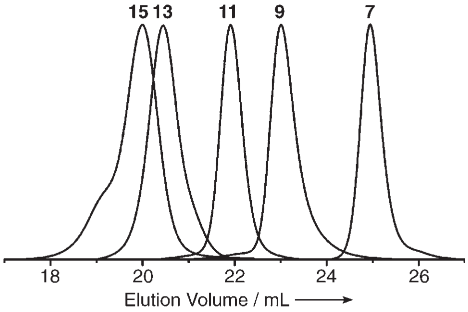


Figure 2. SEC traces for T*i*PS-ethynyl-functionalized polyphenylene dendrimers **7**, **9**, **11**, **13**, and **15** in THF with 500, 10^4, and 10^6 Å column porosities.

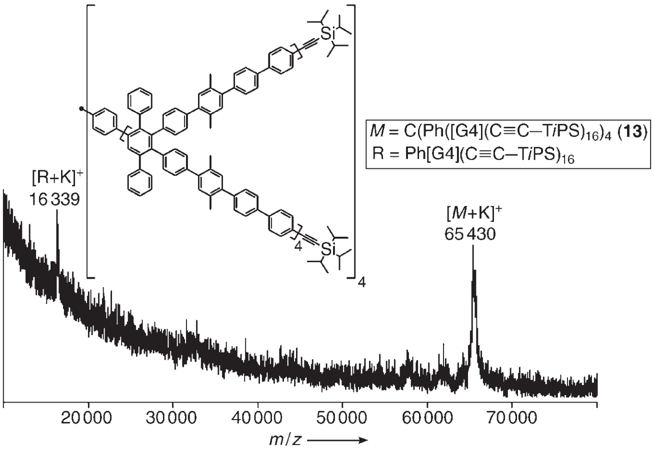


Figure 3. MALDI-TOF mass spectrum (dithranol, potassium trifluoroacetate) of C(Ph([G4](ethynyl-T*i*PS)$_{16}$)$_4$ (**13**); G4 = fourth generation.

fragmentation for this family of dendrimers using these experimental conditions.[18] While fragmentation from MALDI is generally regarded as undesired, the iterative nature of the dendrimer, and a clear fragmentation point (such as at the core) enables conclusive evidence to be drawn from such a "digestion." All the detected ions from this MALDI "digestion," combined with the ^{1}H NMR spectrum of the intact dendrimer **15** unequivocally prove the complete conversion into the fifth generation.

Transmission electron microscopy (TEM; Figure 5, Table 1) and dynamic light scattering (DLS) studies (Table 1) in THF were performed to gauge the sizes of the dendrimers. The TEM samples were obtained by spin-coating dilute CH_2Cl_2 solutions onto freshly cleaved mica substrates and subsequent shadowing with a tungsten/tantalum alloy by electron-beam evaporation at high vacuum, followed by deposition of a thin carbon support.[8,19] The fourth-generation dendrimer **13** showed only filmlike aggregates, but the molecules of fifth-generation dendrimer **15** were well-separated with an average radius of 11.0 nm.[20] There is agreement between the diffusional radius (11.8 nm) and the radius calculated by MMFF94 molecular mechanics (11.0 nm), thus suggesting that the chain ends are not appreciably backfolded and that the shape is preserved in solution. Such agreement, combined with surface accessibility of the chain ends, suggests that the rigid, pentaphenylbenzene branching units provide a conformational stiffness and directionality to the chain ends, similar to that of the parent case.[21] The SEC elution behavior (Table 1) clearly indicates how much more compact the parent polyphenylene dendrimers (**A**, **B**, **C**)[8,16] are than are the new dendrimers **7**, **9**, **11**, **13**, and **15**. The polystyrene (PS)-

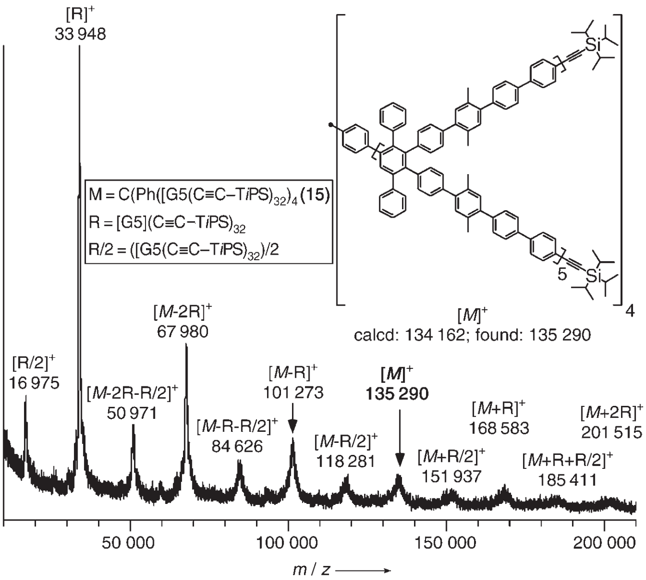


Figure 4. MALDI-TOF mass spectrum (DCTB) of C(Ph([G5](ethynyl-TiPS)$_{32}$)$_4$ (**15**). G5 = fifth generation.

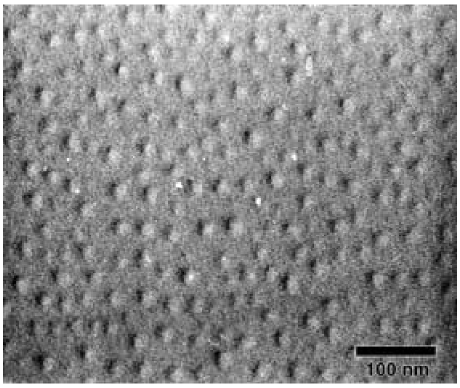


Figure 5. TEM image of tungsten/tantalum-shadowed C(Ph([G5]-(ethynyl-TiPS)$_{32}$)$_4$ (**15**).

equivalent molecular weights (MWs) are less than the masses determined by MALDI-TOF for the former, and with the exception of the fifth-generation dendrimer, the PS-equivalent MWs are higher than the masses (MALDI-TOF) for the new series, thus indicating there is a very large amount of free volume occupied by solvent. Calculation of the dendrimer density (Table 1) from the hydrodynamic volume for each series revealed that a tenfold greater solvent volume is available in the new dendrimers. The significantly faster decrease in the dendrimer density with increasing generation for the new dendrimer series was the result of having used the same compact core from the general polyphenylene dendrimer series. The consequence of such a low dendrimer density could be a higher propensity for interdigitation, and thus aggregates which are difficult to separate.

Experimental and analytical conditions were found up to the fifth generation that demonstrated the complete conversion into the next generation. The limitations of generating molecular ions with MALDI techniques had precluded evaluation of growth to a higher generation with complete certainty, but the results are highly encouraging using MALDI “digestion.” Perhaps the most compelling synthetic observation is that, unlike the syntheses of the parent polyphenylene dendrimers which necessitated several weeks for the final growth reaction to go exclusively to completion, the reaction conversion for the fifth generation required less than 50 h. This result suggests that the steric demands at the chain ends required by the Diels–Alder cycloaddition are well below any critical threshold, completely unlike that of the parent polyphenylene dendrimers. The control over the topology of the branching units and the high porosity result in efficient growth cycles that lead to structural perfection, even for constructions containing 664 and 1368 phenyl rings (for the fourth- and fifth-generation dendrimers **13** and **15**, respectively). To the best of our knowledge, this is the first report of the stepwise chemical synthesis and proof of a truly monodisperse molecule with a diameter greater than 20 nm. Furthermore, no evidence was observed for the physical encapsulation of the branching unit within the dendrimers during the synthesis, thus suggesting that the cavities within the structures are large and may be exploited as novel hosts for large guests.[22] Efforts are underway to evaluate the stiffness and to clarify the aggregate formation for the fifth-generation dendrimer **15**.

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