Divergent Synthesis of Polyphenylene Dendrimers: The Role of Core and Branching Reagents upon Size and Shape

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ABSTRACT: Monodisperse polyphenylene dendrimers up to the fourth generation were synthesized using a divergent growth protocol. By varying the core, dendrimers with dumbbell-, tetrahedral- and propeller-like structures were synthesized. Because of the high-density packing of benzene rings within their branches, these dendrimers are stiff and thus shape persistent. To obtain these dendrimers with a globular shape, a 4-fold (A_4B) dendrimer building unit was introduced. In this case, monodisperse dendrimers are obtained only up to the second generation due to the significantly increased density of benzene rings within the structure. For structure elucidation methods, like MALDI−TOF mass spectrometry, NMR spectroscopy, GPC, VPO, TGA, and DSC were used. Dendrimers of the third and fourth generations were visualized by transmission electron microscopy.

Introduction

Since the first reported synthesis by Vögtle[1] in 1978, dendrimers have received increasing interest, well documented by an exponential growth of published articles.[2] This interest is connected not only to properties such as globular shape and defined size but also to possible applications. They could be used for example as homogeneous catalysts, photosensors, receptors, or molecular complexing agents.[3] The synthesis of dendrimers starts by the addition of building units to a polyfunctional molecule, the "core" of the future dendrimer. The resulting molecule is the first generation of the dendrimer. The multiplicity of the core is defined as the number of building units added to the core and is equal to the number of branches that grow out from the core. After addition, each newly created branch is the starting point for several further sub-branches. The number of branches that grow from a branching point depends on the branching unit. In the case of an A_2B branching unit, it is two, and in the case of an A_4B branching unit, it is four. The further repetitive stepwise buildup results in dendrimers that are therefore highly branched macromolecules with defined (ideally monodisperse) chemical structures.

While highly branched polymers, which are constructed on the basis of amide,[4] ester[5] and ether[6] couplings, dominate the literature, the synthesis of defect-free, branched polyphenylene dendrimers remains a challenge. In contrast to dendrimers containing aliphatic bonds, polyphenylene dendrimers should be stiffer as rotation is only possible around the inter-ring C−C bonds. Furthermore, polyphenylenes were shown to possess in general a high chemical and thermal stability.[7] By comparison with the linear poly-*p*-phenylenes, branched polyphenylenes, including the corresponding dendrimers, should have similar thermal stability but greatly increased solubility, as, due to branching of the polymer, the packing phenomena observed in linear poly-*p*-phenylenes are prevented.[8] Despite these merits, since the initial work by Miller and Neenan,[9] Hart,[10] and Webster,[11] to our knowledge no further work, apart from our own group, on large, highly branched polyphenylene dendrimers has been done so far. However, a similar approach has been adapted by Moore and Xu,[12] who used phenylene−ethynylene dendrimers to obtain stiff macromolecules.

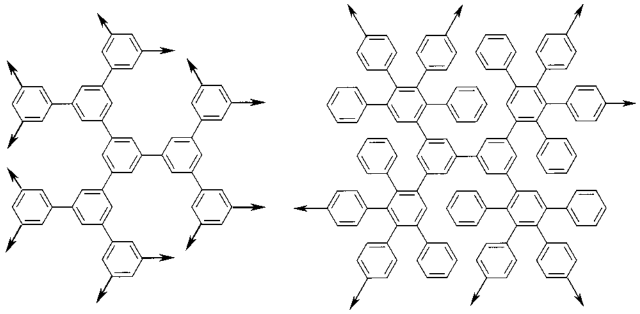

Figure 1. The two known polyphenylene dendrimers, one having 3,5-diarylphenylene repeat units and the other one 2,3,4,5-tetraarylphenylene repeat units. The arrows indicate the direction of growth of the dendrimer branches.

The dendrimers made by Moore and Xu as well as those made by Miller and Neenan are based on 1,3,5-substituted benzenes as branching points. Thus, they exhibit conformational isomers due to rotational mobility around the C−C σ chains. There is a high possibility to flatten these dendrimers to disk-shaped molecules as proved by X-ray analysis. Our dendrimers are based on 1,3,4-substituted benzenes as branching points. It is thus possible to describe them in terms of linear poly(*p*-phenylene) chains (Figure 1). The longest chains start at the core and end at the surface of the molecule. Every two rings, a new, shorter chain starts. As linear polyphenylenes are reasonably stiff, one may safely assume that this is also true for the branches of the dendrimers described in this article. Furthermore, due to the fact that the angle between two polyphenylene chains is always 60° (Figure 1), the distribution of the benzene rings is limited to defined regions within the molecule. Thus, in contrast to the two systems mentioned above, there ought to be some areas within the dendritic structures that are empty and others that are densely populated.

The general concept of our approach to polyphenylene dendrimers has been demonstrated on the first three generations of polyphenylene dendrimers based on the

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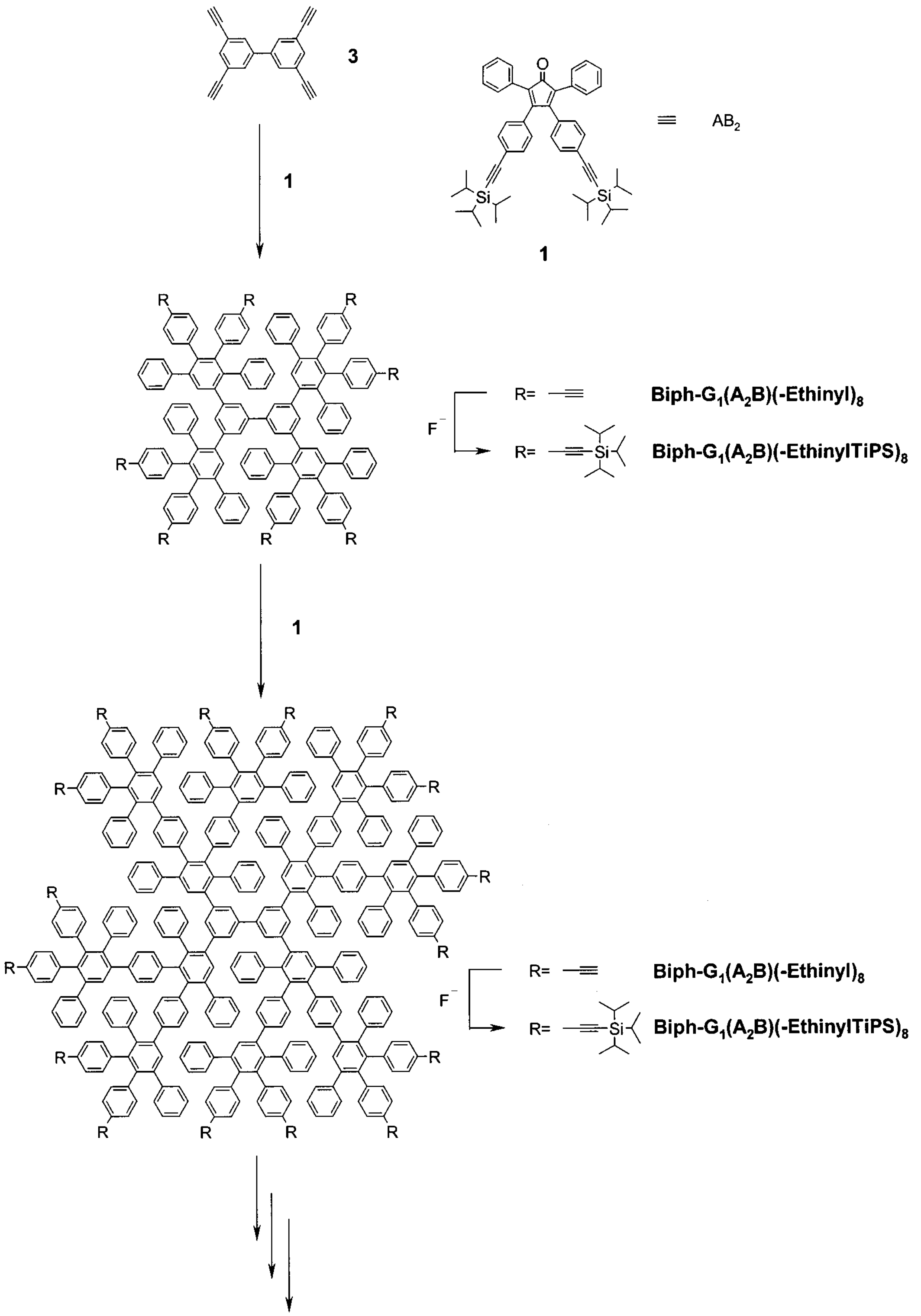
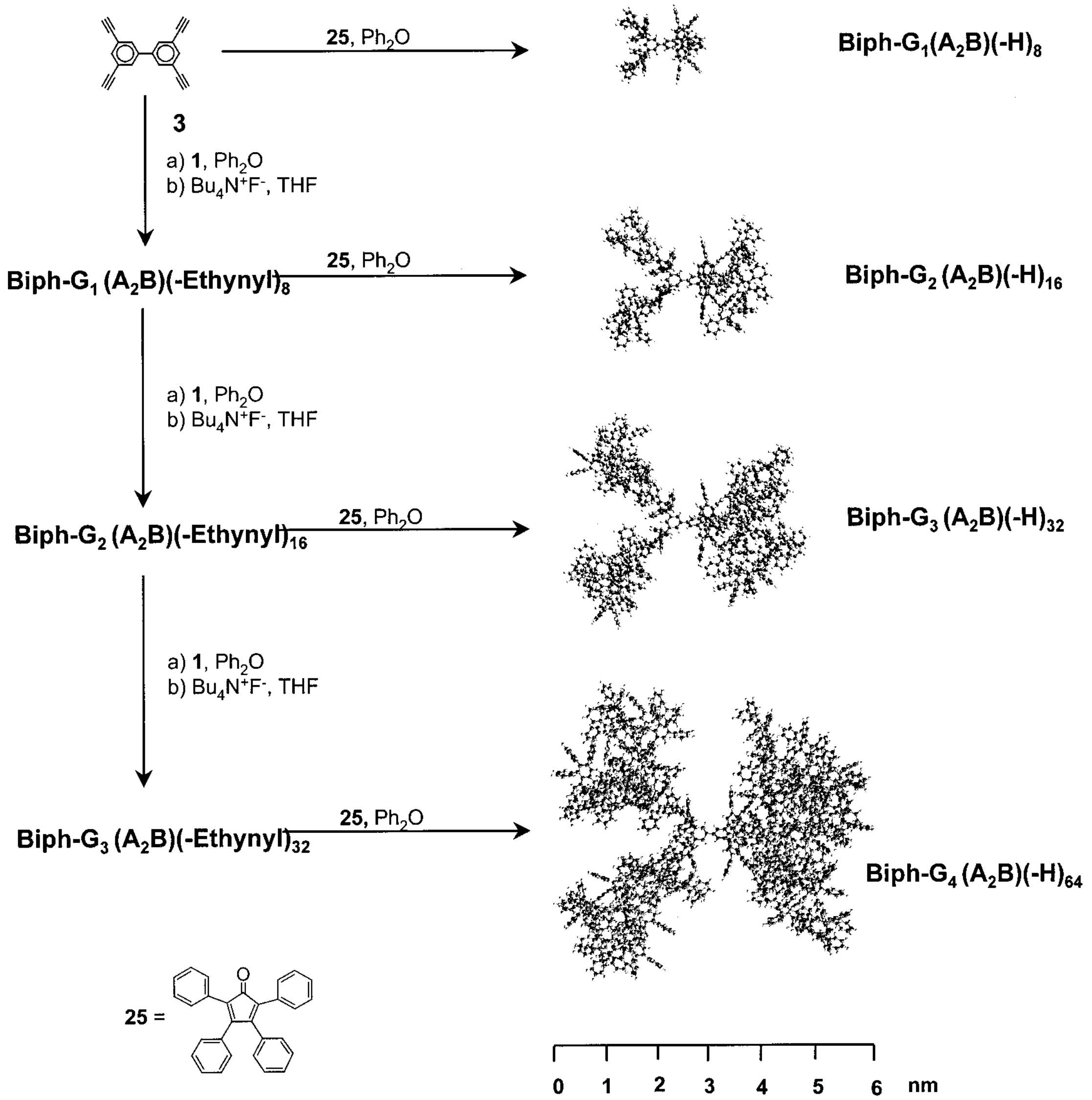
Scheme 1. General Principles for the Synthesis of Dendrimers[a]



[a] The synthesis is based on Diels–Alder cycloaddition of 3,4-bis[4-(triisopropylsilylethynyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (**1**) to the dendrimer followed by the removal of the protecting groups.

biphenyl core which are the subject of previous articles as summarized in Scheme 1.[13] The synthesis of this type of completely aromatic dendrimers is unique in that it is based on the [2 + 4] Diels–Alder cycloaddition of a tetraphenylcyclopentadienone to an ethynyl compound, followed by the elimination of carbon monoxide. This reaction concept originally presented by Dilthey et al.,[14] and studied in detail by Ogliaruso[15] and Ried,[16] involves the addition of tetraphenylcyclopentadienone to a phenylacetylene unit to obtain a pentaphenylbenzene unit. The advantages of this cycloaddition are that it is practically free of side reactions and that the equilibrium is shifted toward the products due to the irreversible loss of CO and the formation of a benzene ring. A retro-Diels–Alder reaction, therefore, cannot occur. This is particularly important in the synthesis of dendrimers as, with growing number of generations, the number of ethynyl functions on the dendrimer and thus the amount of monomer to be added increase exponentially.

Scheme 2[a]



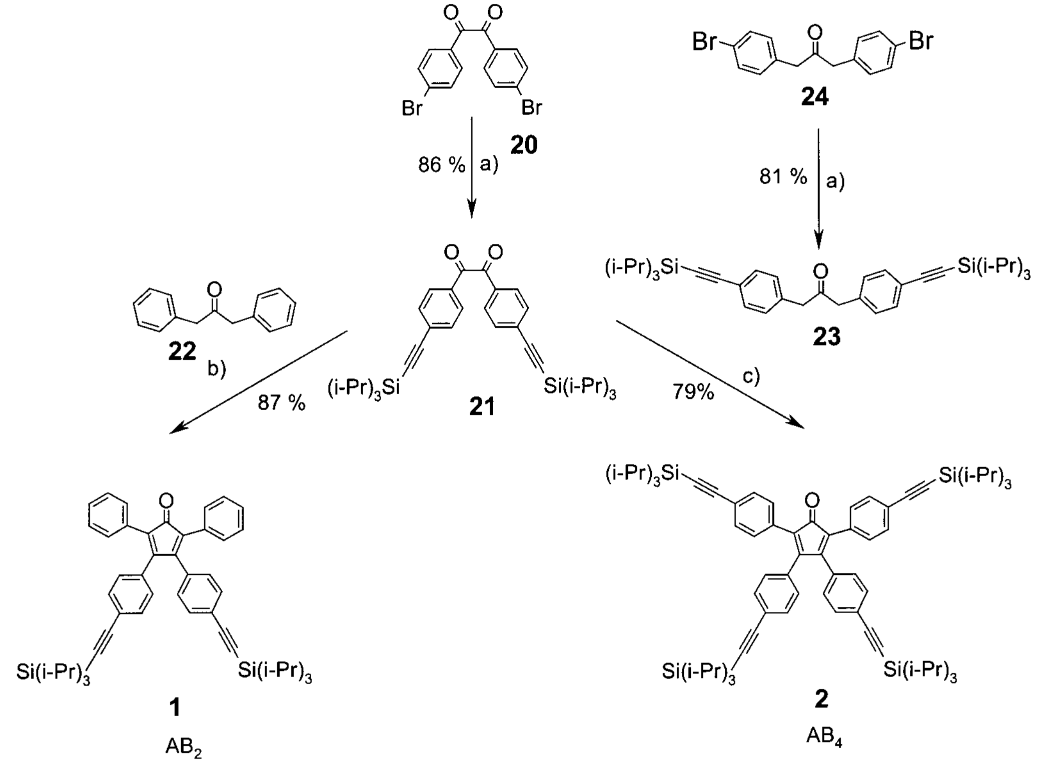
[a] By alternating the addition of the A_2B building unit **1** and the desilylation using ammonium fluoride with catalytic amounts of tetrabutylammonium fluoride starting from the biphenylene core **3**, the synthesis of the ethynyl-substituted biphenylic dendrimers up to the third generation is possible. By adding tetraphenylcyclopentadienone **25** to the ethynyl-substituted dendrimers, the unsubstituted polyphenylene analoges can be obtained up to the fourth generation (space filling models calculated with Cerius^2 molecular modeling package).

In this article, we show how versatile our dendritic concept is for the synthesis of macromolecules with varying size and shape. While the emphasis of this paper is on synthetic aspects, some approaches toward the direct visualization and characterization of these dendrimers are also described. Therefore, we show the synthesis of very large polyphenylene dendrimers with an unprecedented number of benzene rings. Furthermore, we demonstrate the versatility of our approach concerning connectivity and controlling the shape of macromolecules by the use of several cores and branching agents. Finally examples are given of the visualization of some dendrimers by transmission electron microscopy.

Results and Discussion

Synthesis of the Dendrimers. The key step in our dendrimer synthesis is the repeated [2 + 4] cycloaddition of a building block like **1** or **2** to an ethynyl-substituted core or dendrimer and subsequent deprotection. Scheme 2 presents the synthesis of the series of dendrimers based on core **3**. To simplify and optimize the cycloaddition step, we investigated the influences of temperature and solvent on reaction time and product purity. Heating mixtures of ethynyl derivatives and cyclopentadienones under inert atmosphere in different solvents resulted in carbon monoxide elimination at temperatures above 130 °C. The reaction rate of the cycloaddition was influenced not only by the temperature but also by whether the solvent was refluxing or not. At 200 °C, the reaction was complete after 2 h while at 140 °C, 10 h were required when *o*-xylene was used as the solvent and 24 h, when diphenyl ether, 1,4-dichlorobenzene, or 1-methylnaphthalene were employed. The purity of the resulting compounds shown by MALDI−TOF mass spectrometry was, in all cases, the same. The lowered reaction rate obtained by decreasing the reaction temperature was counterbalanced by the simplified reaction procedure. Simple refluxing of reaction components under argon in *o*-xylene gave the pure dendrimer. Compared to that, at 200 °C, the ethynyl derivative dissolved in the solvent had to be

Scheme 3. Synthesis of the Dendrimer Building Blocks 3,4-Bis[4-(triisopropylsilylethynyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (1) and 2,3,4,5-Tetrakis[4-(triisopropylsilylethynyl)phenyl]cyclopenta-2,4-dienone (2)[a]



[a] Key: (a) triisopropylsilylethynyl, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, NEt_3/toluene; (b) Bu_4NOH, *t*-BuOH, 80 °C; (c) KOH, EtOH, 80 °C.

added slowly to the cyclopentadienone solution to prevent the formation of products resulting from incomplete additions. To ensure the full conversion of the ethynyl compound, an excess of the cyclopentadienone was also needed, but could be removed very easily by precipitating the product in ethanol. All the dendrimers are white amorphous powders and were obtained in yields higher than 90% after purification.

To study the properties of polyphenylene dendrimers without the effect of substituents like ethyne or TiPS−ethyne, the unsubstituted analogues were also synthesized (Scheme 2). Therefore, cyclopentadienone **1** had to be exchanged for the parent tetraphenylcyclopentadienone (**25**) in the final cycloaddition step. The substitution of the building block did not influence the addition itself, which could thus be carried out in the same way as for the addition of compound **1**.

The deprotection of the TiPS−ethynyl-substituted dendrimers could be accomplished by using tetrabutylammonium fluoride in tetrahydrofuran (THF). If ammonium fluoride and only catalytic amounts of tetrabutylammonium fluoride in THF or potassium fluoride in DMF were used, purification by column chromatography to remove tetrabutylammonium salts was not necessary. Pure ethynyl-substituted dendrimers were obtained after washing the reaction solution with water and evaporating the solvent.

For the synthesis of the dendrimers on a large scale, the optimization of the synthesis of the A_2B building block was also of major importance. Previously, the Knoevenagel condensation of 4,4′-bis(tri-*iso*-propylsilylethynyl)benzil (**21**) and 1,3-diphenyl-2-propanone (**22**) with KOH in ethanol had afforded yields of around 25%. However, by using tetrabutylammonium hydroxide as base and *tert*-butyl alcohol as solvent, a yield of up to 85% could be obtained. Under these conditions, the reactants are more soluble and side reactions can be prevented (Scheme 3).

To give a clear picture of the growth during synthesis, it should be pointed out that, in the case of branching unit **1**, each monomer (A_2B monomer minus CO and two TiPS protecting groups) contributes 406.5 g/mol to the growth of the dendrimer. That is, addition of four A_2B building blocks to core **3** causes a 1626.0 g/mol mass gain. Extension to the second generation causes a 3252.0 g/mol increase (addition of eight A_2B monomers), i.e., due to the nature of the branching unit, the increase in weight doubles from generation to generation. The fourth-generation dendrimer **Biph−G$_4$(A$_2$B)(−H)$_{64}$**, having the molecular formula $C_{1812}H_{1210}$, has thus a molecular mass of 22 983.53 g/mol. In comparison, the third-generation dendrimer of Miller and Neenan[9] grown from 1,3,5-triphenylbenzene has a total molecular mass of only 1676.2 g/mol. Table 1 summarizes the molecular masses (details below) and the number of benzene rings in the synthesized dendrimers.

The first goal of our synthesis was to determine up to which generation monodisperse dendrimers were obtainable. Up to the third generation, **Biph−G$_3$(A$_2$B)(−EthynylTiPS)$_{32}$** dendrimers which were pure according to MALDI−TOF mass spectrometry and NMR spectroscopy had been obtained. Starting from this point, the deprotection of **Biph−G$_3$(A$_2$B)(−EthynylTiPS)$_{32}$** by the procedure described above was carried out to give pure **Biph−G$_3$(A$_2$B)(−Ethynyl)$_{32}$**. While treating this compound with the A_2B building unit **1**, the steric crowding of the TiPS−ethynyl group became so large that in situ deprotection occurred leaving the ethynyl groups vulnerable to further cycloaddition. In contrast, the addition of tetraphenylcyclopentadienone

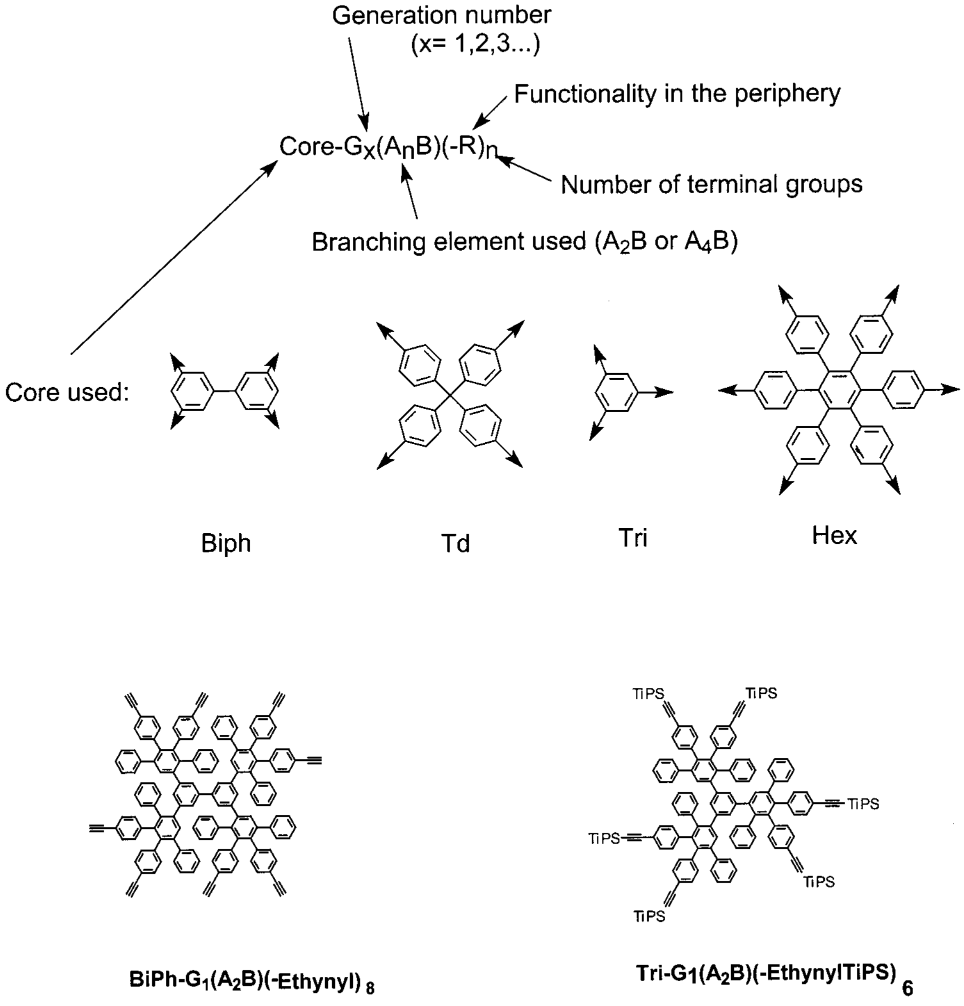


Figure 2. Nomenclature of polyphenylene dendrimers.

Table 1. Molecular Formula, Calculated Mass, Mass Determined by MALDI−TOF Mass Spectrometry, and Number of Phenylene Rings Contained within the Dendrimers

compound, generation	mol formula	molecular mass (g/mol)		no. of benzene rings
		calcd	measd	
Biph−$G_1(A_2B)(-H)_8$	$C_{132}H_{90}$	1676.2	1676.6	22
Biph−$G_2(A_2B)(-H)_{16}$	$C_{372}H_{250}$	4720.1	4719.2	62
Biph−$G_3(A_2B)(-H)_{32}$	$C_{852}H_{570}$	10807.9	10803.6	142
Biph−$G_4(A_2B)(-H)_{64}$	$C_{1812}H_{1210}$	22983.5	22983.1	302
Td−$G_2(A_2B)(-H)_{16}$	$C_{385}H_{260}$	4886.3	4877	64
Td−$G_3(A_2B)(-H)_{32}$	$C_{385}H_{580}$	10974.1	11 006	144
Td−$G_4(A_2B)(-H)_{64}$	$C_{1825}H_{1220}$	23149.8	23 217	304
Tri−$G_1(A_2B)(-H)_8$	$C_{96}H_{66}$	1219.6	1220.3	16
Tri−$G_2(A_2B)(-H)_{16}$	$C_{276}H_{186}$	3502.5	3501.4	46
Hex−$G_1(A_2B)(-H)_8$	$C_{222}H_{150}$	2817.6	2816.4	37
Hex−$G_2(A_2B)(-H)_{16}$	$C_{582}H_{390}$	7383.5	7382.5	97
Biph−$G_2(A_4B)(-H)_{64}$	$C_{612}H_{410}$	7764.0	7767.8	102
Td−$G_2(A_4B)(-H)_{64}$	$C_{625}H_{420}$	7930.2	7928.9	104

(**25**) yielded exclusively the fourth-generation **Biph−$G_4(A_2B)(-H)_{64}$** as a monodisperse polyphenylene containing 302 benzene rings (Figure 3). This result can be attributed to the very high degree of crowding reached in the outer shell of the dendrimer branches. While there was enough space to accommodate 32 tetraphenylcyclopentadienones, the space was too limited for the inclusion of 64 further TiPS−ethynyl groups which are contained in 32 A_2B building blocks. Nevertheless, it appears that it is possible to synthesize high mass monodisperse dendritic polyphenylene macromolecules up to the fourth generation with astonishing reliability. Furthermore, these results are in accordance with the theory by de Gennes and Harvet stating that the density of the outer shell of a dendrimer increases from generation to generation until it reaches a point where monodisperse growth becomes impossible.[17]

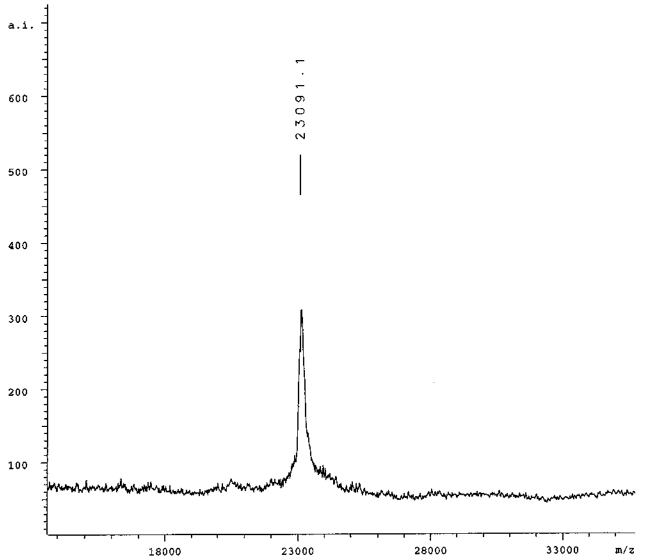
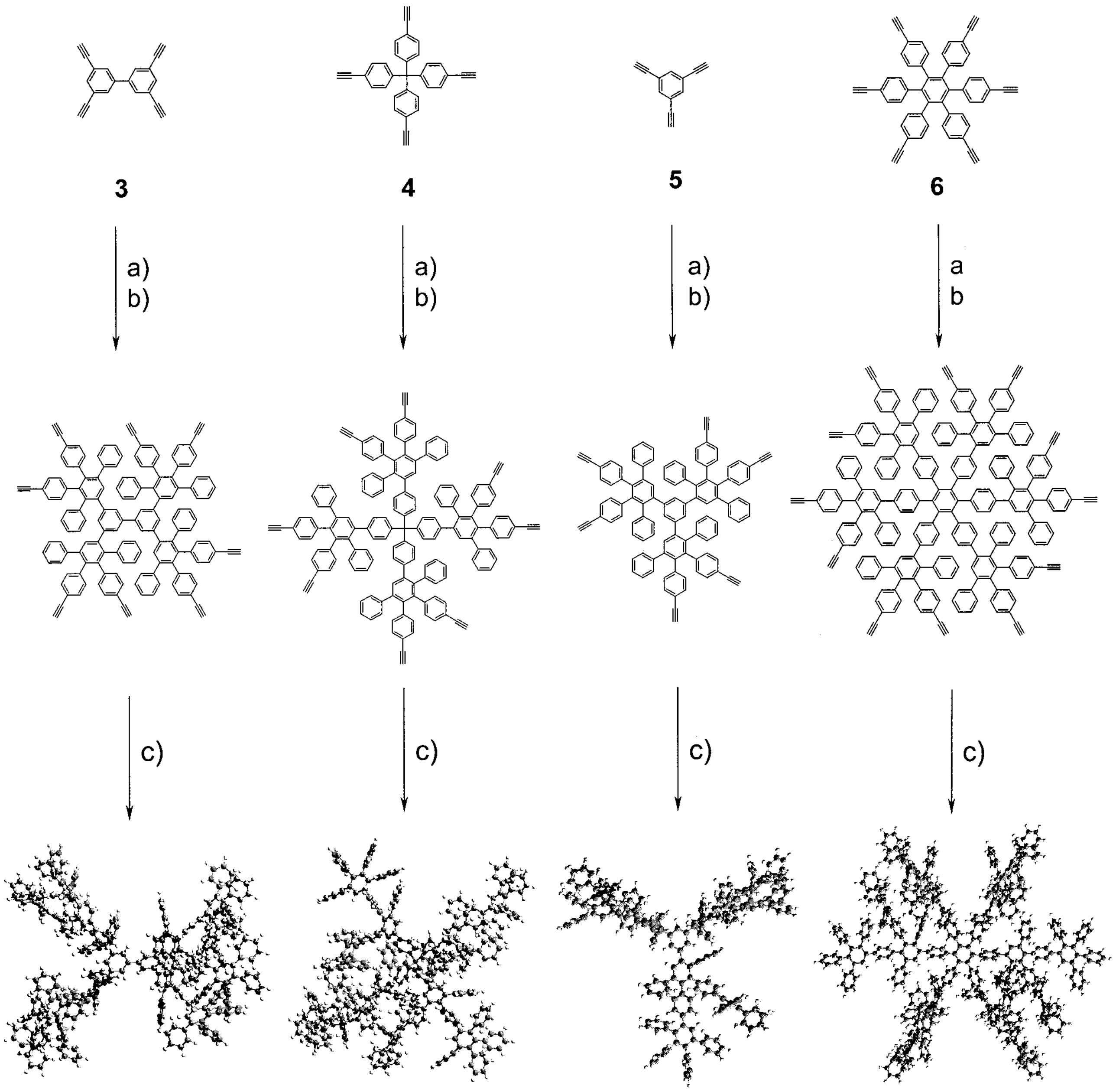


Figure 3. MALDI−TOF mass spectrum of **Biph−$G_4(A_2B)(-H)_{64}$**. The calculated molecular mass of $[C_{1812}H_{1210}, Ag]^+$ **(Biph−$G_4(A_2B)(-H)_{64}$)** is 23091.4 Da.

Scheme 4. Cores and Space Filling Models[a] **of the Corresponding Second Generation Dendrimers**[23]



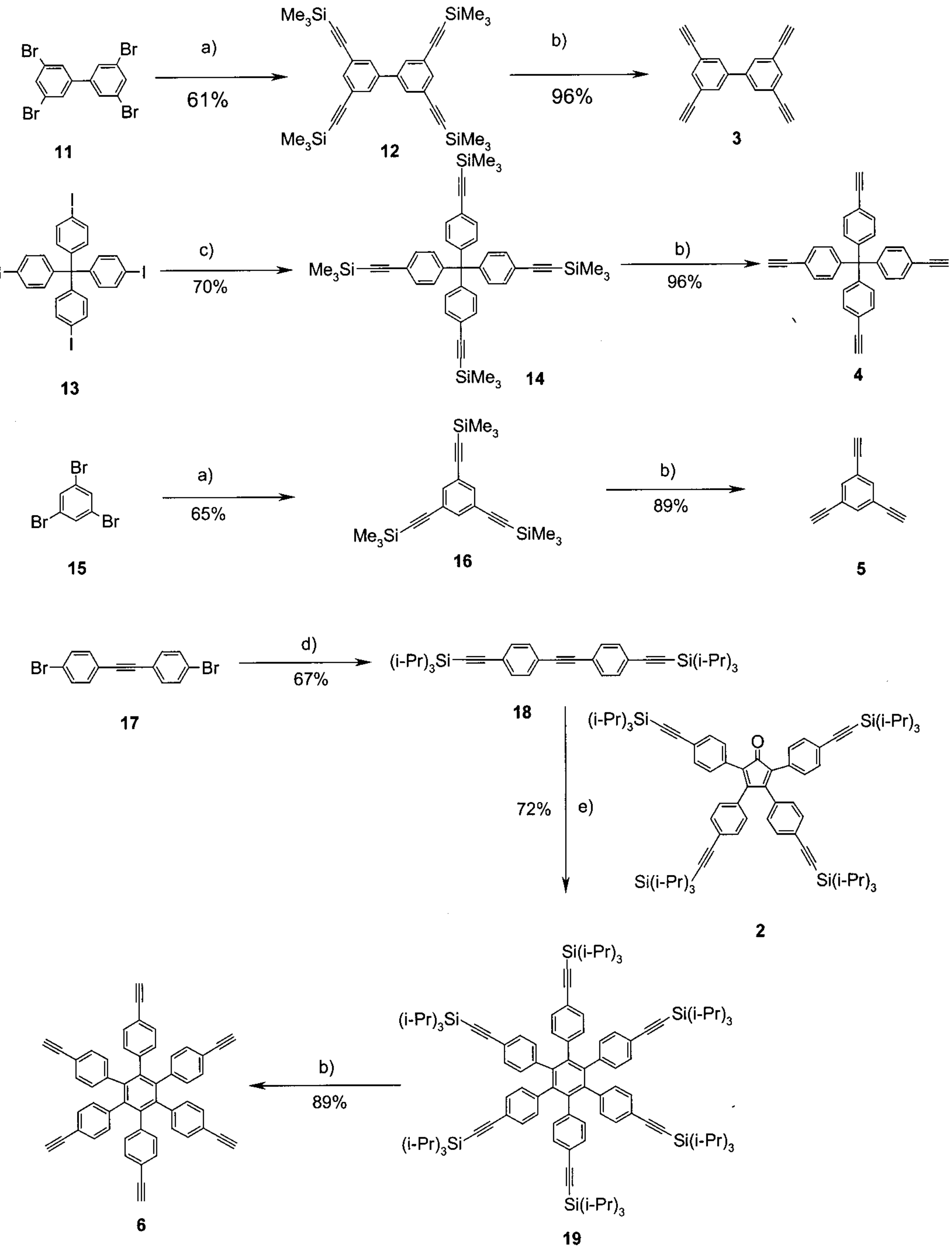
[a] Key: (a) **1**, *o*-xylene, reflux; (b) NH_4F, Bu_4NF, THF; (c) **25**, *o*-xylene, reflux).

To study the influence of the core on the shape of the dendrimer, the series based on tetrakis(4-ethynylphenyl)-methane (**4**), 1,3,5-triethynylbenzene (**5**), and hexakis-(4-ethynylphenyl)benzene (**6**) were synthesized in addition to the one based on 3,3′,5,5′-tetraethynylbiphenyl (**3**). Initially, for the examination of the influence of the core on the dendritic structure, four ethynyl-substituted cores with different symmetries were synthesized.

The variation of the cores should cause the branches to grow in certain given directions (see Scheme 4). Biphenyl core **3** has four ethynyl functional groups in the 3, 3′, 5, and 5′ positions, promoting a kind of C_2 symmetry of the dendrimer with rotational freedom around the aryl−aryl bond of core **3**. Using the tetraphenylmethane core **4**, growth can extend to the four corners of an ideal tetrahedron. In contrast to core **3**, where rotation around the central bond of the biphenyl core is possible, in the case of **4** a more rigid structure of the dendrimer is expected, which is necessary for a shape-persistent macromolecule. The 1,3,5-triethynylbenzene core (**5**) and hexakis(4-ethynylphenyl)benzene core (**6**) should promote an anisotropic extension within the plane of the central phenylene ring, since the principal oligo(*p*-phenylene) axes of all the branches grow in this plane.

The cores **3**, **4**, and **5** were synthesized via the palladium-catalyzed coupling of trimethylsilylethyne with 3,3′,5,5′-tetrabromobiphenyl (**11**),[18] tetrakis(4-iodophenyl)methane (**13**),[19] and 1,3,5-tribromobenzene (**12**),[20] respectively, using the Hagihara method.[21] The trimethylsilyl protecting groups were removed using potassium fluoride in DMF. Core **6** (with six arms) was the product of a Diels−Alder reaction between the A_4B unit **2** (*vide infra*) and 4,4′-bis(tri-*iso*-propylsilylethynyl)-diphenylethyne (**18**) and subsequent treatment with tetrabutylammonium fluoride to cleave the TiPS groups

Scheme 5. Synthesis of the Biphenylene Core 3, Tetraedric Core 4, Trigonal Core 5, and Hexagonal Core 6[a]



[a] Key: (a) trimethylsilylethynyl, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, NEt_3/toluene, 80 °C; (b) Bu_4NF, THF, room temperature; (c) trimethylsilylethynyl, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, NEt_3/toluene, room temperature; (d) triisopropylsilylethynyl, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, NEt_3/toluene 80 °C; (e) Ph_2O, 200 °C.

(Scheme 4). Compound **18** was synthesized via palladium-catalyzed coupling of 4,4′-dibromodiphenylacetylene (**17**) and TiPS−ethyne (Scheme 5).

The synthesis of the first four generations based on **4** supports the result found for the biphenyl case. Here, the synthesis of the first three generations was also possible by the protocol described above. Again, however, the treatment of **Td−G$_3$(A$_2$B)(−Ethynyl)$_{32}$** with the A_2B building block showed a mixture of products containing not only the desired fourth generation but also side products resulting from an in situ deprotection and a further addition of the monomer. Nevertheless, the unsubstituted third generation could be prepared when **Td−G$_3$(A$_2$B)(−Ethynyl)$_{32}$** was treated with **25**. In addition to the dendrimer series based on **3** and **4** the series based on the cores **5** and **6** were synthesized. Here the synthesis of the first two generations has been carried out so far. Their preparation is as straightforward as for the series based on cores **3** and **4**.

The second factor expected to influence the shape of the dendrimers is the degree of branching of the branching units. The more branches emanate from a branching point, the higher the degree of crowding will become. For this reason, in addition to the A_2B branching unit **1**, which allows growth of two branches per junction, the A_4B unit **2** was synthesized.

In contrast to the A$_2$B branching unit **1**, the A$_4$B branching unit **2** was prepared in 80% yield from 4,4′-bis(tri-*iso*-propylsilylethynyl)benzil (**21**) and 1,3-bis[4-(tri-*iso*-propylsilylethynyl)phenyl]acetone (**23**) in ethanol, using potassium hydroxide as base. The acetone derivative **23** was obtained by the Hagihara coupling[21] of bis(4-bromophenyl)acetone (**24**) with TiPS−ethyne. Compound **24** was, in turn, synthesized by the reaction of 4-bromobenzyl bromide with ironpentacarbonyl (Scheme 3).[22]

Applying **2** in our dendrimer synthesis together with the cores **3** and **4**, it was possible to obtain the first-generation dendrimers **Biph−G$_1$(A$_4$B)(−EthynylTiPS)$_{16}$** and **Td−G$_1$(A$_4$B)(EthynylTiPS)$_{16}$**. However, further addition of the A$_4$B branching unit **2** to the deprotected dendrimer **Biph−G$_1$(A$_4$B)(−Ethynyl)$_{16}$** resulted in a polydisperse product consisting mainly of the 14-fold addition product[23] though traces of the desired 16-fold addition product were also found. This phenomenon may be explained by the extreme crowding of the phenylene rings within the dendrimer which does not allow the accommodation of **16** further A$_4$B building units. Furthermore, tetraphenylcyclopentadienone (**25**) reacts with **Biph−G$_1$(A$_4$B)(−Ethynyl)$_{16}$** to form the 16-fold addition product exclusively, supporting the above assumption. Likewise it was possible to treat **Td−G$_1$(A$_4$B)(−EthynylTiPS)$_{16}$** with 16 tetraphenycyclopentadienones (**25**) thus successfully producing **Td−G$_2$(A$_4$B)(−H)$_{64}$**. This result should be compared with the synthesis of the fourth-generation moieties **Biph−G$_4$(A$_2$B)(−H)$_{64}$** and **Td−G$_4$(A$_2$B)(−H)$_{64}$**. While in the latter case, the synthesis of the substituted generations was only just prevented by steric crowding and the fourth generation as such was present, but underwent further additions, the increase in the A$_4$B case was so immense that not even all ethynyl groups of the first generation could react. This may be understood, when one considers that in the case of the dendrimers where the A$_4$B monomer **2** was used, the number of branching points was not just doubled with each new generation but quadrupled. Thus, the second-generation dendrimers have a molecular mass increase of 5703.5 g/mol resulting in molecular masses of 7764.0 and 7930.2 g/mol for **Biph−G$_2$(A$_4$B)(−H)$_{64}$**, and **Td−G$_2$(A$_4$B)(−H)$_{64}$**, respectively. The unsubstituted third generations would therefore have to accommodate 422 and 424 benzene rings and have molecular weights of 32 115 and 32 270, respectively.

In conclusion, synthesis of monodisperse polyphenylene dendrimers is possible in high yield and purity up to the fourth generation for the A$_2$B building unit. This limitation is independent of the core, which suggests that growth defects occur due to steric crowding within the branches. Nevertheless this synthetic method opens the way to monodisperse macromolecules with molecular masses higher than 20 000 g/mol.

Physical Properties and Characterization. All the dendrimers prepared above are colorless, easily soluble in a range of solvents such as tetrahydrofuran, dichloromethane, or toluene, and insoluble in hexane and ethanol or methanol and therefore easily precipitable, making workup very simple. The higher the number of generations of a dendrimer, the more soluble it becomes. Whereas **Td−G$_4$(A$_2$B)(−H)$_{64}$** and **Td−G$_3$(A$_2$B)(−H)$_{32}$** are soluble to concentrations up to 40 wt % in chlorinated solvents such as tetrachloroethane, the solubility of **Td−G$_2$(A$_2$B)(−H)$_{16}$** is much lower and **Td−G$_1$(A$_2$B)(−H)$_8$** is practically insoluble. Solvent is situated inside of the dendrimer, placed between the branches and not just around the dendrimer. This makes drying difficult and tends to falsify elemental analyses.

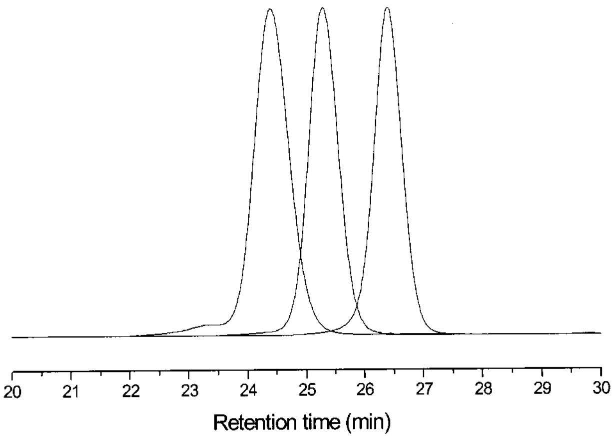


Figure 4. Size-exclusion chromatographs of **Td−G$_2$(A$_2$B)(−H)$_{16}$**, **Td−G$_3$(A$_2$B)(−H)$_{32}$**, and **Td−G$_4$(A$_2$B)(−H)$_{64}$**.

MALDI−TOF mass spectrometry proved particularly useful in the characterization of the dendrimers. Using this established method for the determination of purity and structural integrity of polymers,[24] we were also able to determine the monodispersity of the dendrimers (Figure 3). Potential defects, resulting from incomplete [2 + 4] cycloaddition during dendrimer growth, could be unequivocally detected, because each unreacted ethynyl group resulted in a mass difference of 717 (A$_2$B branching unit minus CO) or 1077 g/mol (A$_4$B branching unit minus CO).

Figure 3 shows the MALDI−TOF mass spectrum of the fourth-generation dendrimer **Biph−G$_4$(A$_2$B)(−H)$_{64}$**. The spectrum was recorded in the presence of silver cations. A single molecular peak at 23 091.1 g/mol (mass of molecule + mass of silver cation) is observed for **Biph−G$_4$(A$_2$B)(−H)$_{64}$**. This value is in very good correspondence with the mass calculated for $C_{1812}H_{1210}Ag$ (23 091.4 g/mol). The absence of any peaks pointing to the incomplete addition of tetraphenylcyclopentadienone demonstrates the completion of the cycloaddition reaction.

Size exclusion chromatography (SEC) is also a useful tool in the analysis of the molecular mass and the dispersity of the resulting dendrimers. Figure 4 presents the eluogram of dendrimers **Td−G$_2$(A$_2$B)(−H)$_{16}$**, **Td−G$_3$(A$_2$B)(−H)$_{32}$**, and **Td−G$_4$(A$_2$B)(−H)$_{64}$**. As expected, the molecular masses based on polystyrene standards, calculated from the SEC traces are lower than the nominal masses and the differences increase with increasing molecular mass.[25] This we interpret as due to the adoption of a more globular shape compared to polystyrene. The higher the molecular masses of the dendrimers are, the shorter the retention times on the SEC column. For higher generation dendrimers, small shoulders can be seen on the molecular peaks in the SEC due to the fact that aggregation of the dendrimers is possible. A covalent linkage between dendrimers can be excluded due to the fact that in MALDI−TOF, the only signals which can be seen at higher molecular masses, can be attributed to cluster formation. The M_w/M_n ratio obtained by SEC is found to be between 1.03 and 1.05, which is characteristic for monodisperse dendrimers.[26] Compared to MALDI−TOF mass spec-

Table 2. Molecular Weights Measured via Vapor Pressure Osmometry, Gel-Permeation Chromatography and MALDI−TOF Mass Spectrometry for Td−$G_2(A_2B)(-H)_{16}$ Td−$G_3(A_2B)$(-H)$_{16}$ Td−$G_4(A_2B)(-H)_{16}$

	VPO	GPC			molecular mass (g/mol)	
	M_n	M_n	M_d	M_w/M_n	measd[a]	calcd
Td−$G_2(A_2B)(-H)_{16}$	4900	3900	4000	1035	4984	4882
Td−$G_3(A_2B)(-H)_{32}$	9500	7900	8150	1029	11 113	10 978
Td−$G_4(A_2B)(-H)_{64}$	13 800	13 780	14 500	1052	23 324	23 170

[a] MALDI−TOF MS [M^+Ag^+].

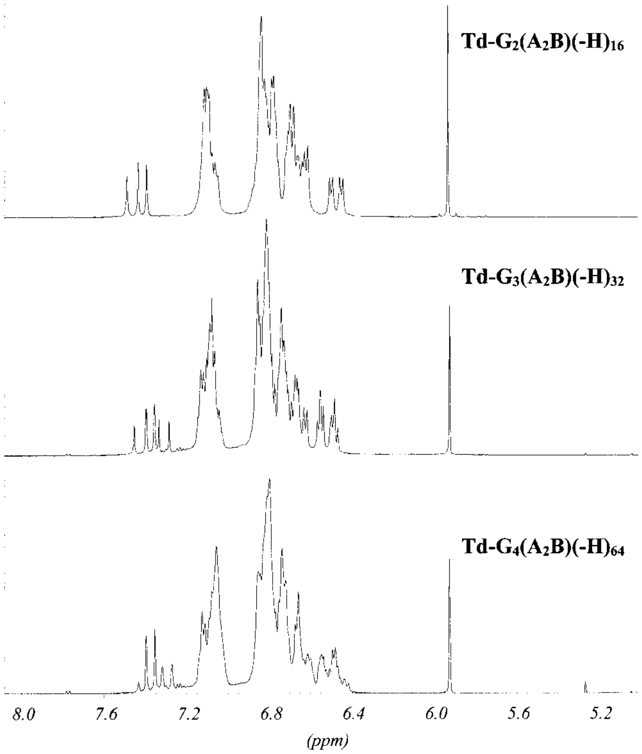


Figure 5. ^{1}H NMR spectrum (500 MHz, C2D2Cl4) of the dendrimers **Td−$G_2(A_2B)(-H)_{16}$**, **Td−$G_3(A_2B)(-H)_{32}$**, and **Td−$G_4(A_2B)(-H)_{64}$**.

trometry, results obtained from SEC give only qualitative answers about the dimension and the purity because the resolution of SEC is not high enough to detect small defects on the dendrimers.[25] Very good agreement between nominal molecular masses and measured ones is given by vapor pressure osmometry (Table 2). Whereas for the second-generation dendrimer **Td−$G_2(A_2B)(-H)_{16}$** the measured mass corresponds very well to the nominal ones, for higher generations, the masses are lower due to the experimental limitations of this method for high molecular masses.[27]

Because of the large number of different aromatic hydrogen atoms, ^{1}H NMR spectroscopy gives only limited information about structure and purity of the dendrimers synthesized. However, in the case of the tetrahedral series dendrimers **Td−$G_2(A_2B)(-H)_{16}$** to **Td−$G_4(A_2B)(-H)_{64}$** and also in the case of the dendrimers based on cores **5** and **6**, the singlets shifted toward low-field with respect to $\delta = 7.25$ ppm are assigned to the protons on the central ring of the pentaphenylbenzene units. Furthermore, these resonance signals are also assigned to the different generation layers within a dendrimer (Figure 5). For example, the spectrum of **Td−$G_2(A_2B)(-H)_{16}$** shows one singlet at $\delta = 7.49$ ppm for the four equivalent protons of the first-generation pentaphenylbenzene units and two singlets at $\delta = 7.43$ and 7.39 ppm for the eight protons of the second-generation pentaphenylbenzene units. The spectrum of dendrimer **Td−$G_3(A_2B)(-H)_{32}$** has seven singlets, partially overlapping, corresponding to the 28 protons of the three generations in this dendrimer. Further structural information could not be obtained due to strong overlap of the signals in the aromatic region. However, in the case of the ethynyl- and TiPS−ethynyl-substituted dendrimers, the ratio of the aromatic to the aliphatic signals corresponds to the expected structure.

To obtain some information about the stiffness of our polyphenylene dendrimers, they were subjected to solid-state NMR experiments. This experiment should give information about the dynamics and therefore the mobility of different parts of the dendrimer. For the detection of slow dynamics within the dendrimer, static ^{13}C Exchange and CODEX (centerband-only detection of exchange) experiments have been applied in cooperation with Spiess et al.[28] They show that our polyphenylene dendrimers are surprisingly rigid dendrimers and that slow dynamic processes are limited to local flip motions of single phenyl rings with flip frequencies of 10 Hz. Spiess et al.[29] have also demonstrated that the mobility of the dendrimer increases with each further generation. This may be an explanation for the observed better solubility of higher generation dendrimers. These experiments also reveal that dendrimers based on the tetrahedral core, like **2**, are less mobile than those based on the biphenyl core, like **15**, which shows mobility along the inner biphenyl bond of the core. Fast motional processes with correlation times on the nanosecond scale were characterized by ^{13}C−^{1}H multiple-quantum spectroscopy. These motional processes can be attributed to 60° vibration of phenyl groups around their linking bond.

Because of the polyphenylene structure, these dendrimers have a high thermal stability. Degradation under nitrogen occurs in the unsubstituted dendrimers at temperatures above 500 °C according to thermogravimetric analysis and at temperatures above 200 °C for the ethynyl- and TiPS−ethynyl-substituted dendrimers. No glass transition or other phase changes were observed by DSC in any dendrimers up to the decomposition temperature. Their chemical stability is also noteworthy. Boiling in concentrated hydrochloric acid solution and in 9 M potassium hydroxide solution for 7 days fails to show any decomposition of the dendrimers. Substitution experiments showed that they react only with strong electrophiles, such as sulfuric acid, by aromatic electrophilic substitution, but without change of the polyphenylene framework.

Visualization and Simulation. Dendrimers have been the focus of interest not only due to their monodispersity at high molecular masses but also due to their three-dimensional structure. In particular, the influence of the macromolecular structure on the shape of dendrimers and dendritic structures is in the center of investigation by a number of groups.[30] The first theoretical works presented by de Gennes and Hervet stated that at high generations dendrimers tend to have globular shape, due to steric crowding at the terminal branches, and their terminal reactive groups should be situated on the surface of this globulae.[17] Therefore, a number of studies, like NMR,[31] fluorescence depolarization,[32] small-angle X-ray or neutron scattering (SAXS

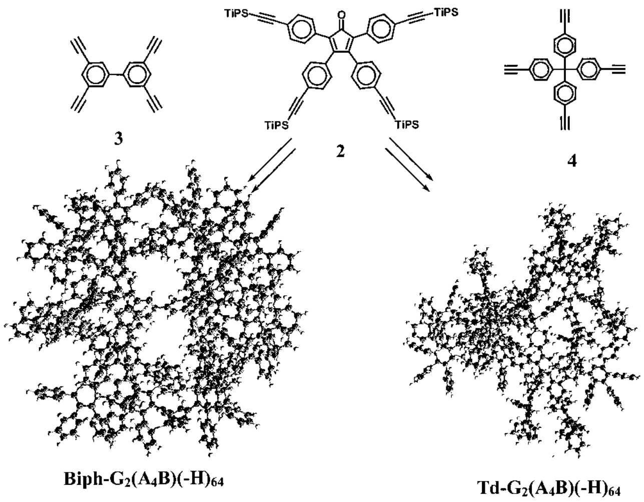


Figure 6. Building blocks and molecular mechanics models of the dendrimers **Biph−G$_2$(A$_4$B)(−H)$_{64}$** and **Td−G$_2$(A$_4$B)(−H)$_{64}$**.

or SANS),[33] and transmission electron microscopy (TEM)[34] have been done to elucidate the real shape of dendrimers.

First impressions about the shape and the size of polyphenylene dendrimers can be obtained by molecular-mechanics-simulations. Scheme 3 shows three-dimensional representations of the second generations of the dendrimers grown using the A$_2$B building unit **1**. The models were obtained using the Cerius^2 molecular modeling package (MM2 85 Forcefiled, Conjugate Gradient 200 Algorithm). Dendrimers based on the biphenyl core **3** lead to the dumbbell shape, as presented in a previous article.[38b] The diameter, taken from the two carbon atoms furthest apart, is about 2 nm for the first generation.

Td−G$_2$(A$_2$B)(−H)$_{16}$, based on the tetrahedral core **4**, shows a tetrahedral molecular shape which resembles the shape of the core very well. Because of the large number of benzene rings around the central methane unit, the branches are hindered in their rotation (Scheme 3), lowering the internal mobility of the molecule compared to **Biph−G$_2$(A$_2$B)(−H)$_{16}$**.[38a] According to the simulations of Bredas et al.,[38a] the dendrimers based on core **5** and core **6** adopt a propeller structure.[38a]

As indicated by the simulations, the dendrimers based on the A$_4$B branching unit **2** tend to adopt a spherical form already at lower generations indifferent of the core (Figure 6). This makes sense when considering the chemical structure of these molecules. As in the case of their A$_2$B analogues, the length of their branches grows by only two phenylene rings per generation. The similarity of the molecular dimensions of A$_4$B- and A$_2$B-grown dendrimers was confirmed by light-scattering experiments. It was shown that both molecules possess a hydrodynamic radius of 1.9 nm.[35] These values are in very good agreement with those estimated from the models obtained by the simulations.[36] However, in both cases shown here, the A$_4$B dendrimers contain about 65% more benzene rings within the same space. Considering that the molecular diameters are the same in both cases, one can conclude that the use of the A$_4$B monomer (**2**) leads to a remarkable increase in the overall density of the molecule. The chemical structure does also show that the branches grow somewhat more evenly into all directions when compound **2** is used as the branching agent, leading ultimately to a more spherical structure as well in contrast to **1**, which just causes growth away from the core.

Experimental evidence about the shape of the dendrimer can be obtained by direct visualization methods, like atomic force microscopy (AFM) or TEM. AFM, subject of a parallel publication,[37] gives results that show the radii determined for our dendrimers to correspond very well with the values gained from the models obtained previously by means of molecular mechanics and dynamics approaches (Cerius^2 molecular modeling package).[38] The radius was taken to be the length of the oligo(*p*-phenylene) axis in the center of each branch spanning the core to the surface. The first-generation dendrimers were estimated by AFM to have diameters of about 2.5 nm and the second, third, and fourth to have diameters of about 3.8, 5.1, and 6.4 nm, respectively.[39]

A more obvious impression of the shape of third- and fourth-generation dendrimers is given by transmission electron microscopy. Dendrimers of various kinds have already been investigated in the ordered solid state[34c] but owing to their expected size electron micrographs of isolated dendrimers are rare. One reason might be that the experimentalists were faced with the fundamental problem of electron microscopical investigation, namely to discriminate the isolated molecules from the surroundings. Jackson, Chanzy, and co-workers[34a] found for their system a selective positive stain. We have studied tungsten/tantalum shadowed samples of **Td−G$_3$(A$_2$B)(−H)$_{32}$**, **Td−G$_4$(A$_2$B)(−H)$_{64}$**, and **Biph−G$_4$(A$_2$B)(−H)$_{64}$**. The samples were prepared in such a way that the single molecules lie isolated from each other on the surface. Typical micrographs of the samples are displayed in Figure 7. **Td−G$_3$(A$_2$B)(−H)$_{32}$** can be described sufficiently well as spherical. To some extent this is also true for the **Td−G$_4$(A$_2$B)(−H)$_{64}$** molecules, but in general the shapes of dendrimers of the fourth-generation **Td−G$_4$(A$_2$B)(−H)$_{64}$** and **Biph−G$_4$(A$_2$B)(−H)$_{64}$** look rather irregular. However, one has to take into account that the shape seen on an electron micrograph is a projection of a three-dimensional object in the direction of the beam path. After preparation by spin coating, the dendrimer molecules occupy various orientations by chance and their outer contours look different according to the respective projection. For over more than 250 molecules of each species inspected, one has the impression that the dendrimers with tetrahedral core face the incoming tungsten/tantalum alloy with a higher cross section than the species with the biphenyl core, where mainly the edges became emphasized by metal shadowing.

The size of the dendrimers cannot be determined unambiguously. For a statistical evaluation we describe their size by the diameter of a circle about each molecule as the basic data for the histograms displayed in Figure 8. In evaluating the size distribution of the fourth-generation dendrimers, one is faced with the recognition problem of whether one has to treat an object as one molecule or a superposition of at least two. Together with the multiplicity of possible orientations of the huge molecules owing to the increase in conformers the half-width of the resulting Gaussians is rather wide. The mean values for **Td−G$_3$(A$_2$B)(−H)$_{32}$**, **Td−G$_4$(A$_2$B)(−H)$_{64}$** and **Biph−G$_4$(A$_2$B)(−H)$_{64}$** are 5.2, 6,1, and 5.3 nm, respectively, which are in reasonable agreement with the corresponding values determined from AFM measurements and calculations of molecular mechanics.

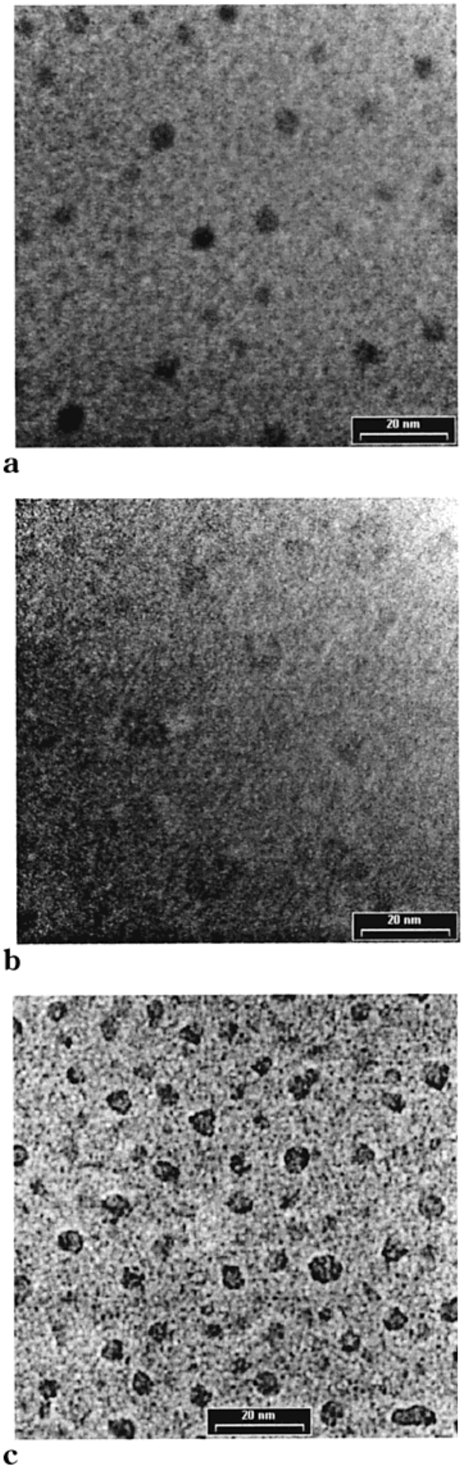


Figure 7. Transmission electron micrographs of **Td−G$_3$(A$_2$B)(−H)$_{32}$** (a), **Td−G$_4$(A$_2$B)(−H)$_{64}$** (b), and **Biph−G$_4$(A$_2$B)(−H)$_{64}$** (c).

Attempts isolating dendrimers of high generation during the electron microscopical preparation meet with problems. Owing to the rotational mobility of parts of the molecules around single bonds, the dendrimers tend to entangle themselves. It should be mentioned that in the very beginning of our TEM investigations an attempt to spread a diluted solution of **Biph−G$_4$(A$_2$B)(−H)$_{64}$** onto water led to a self-supporting film of the dendrimers in which structural details could not be separated from features of the contrast transfer function of the instrument.

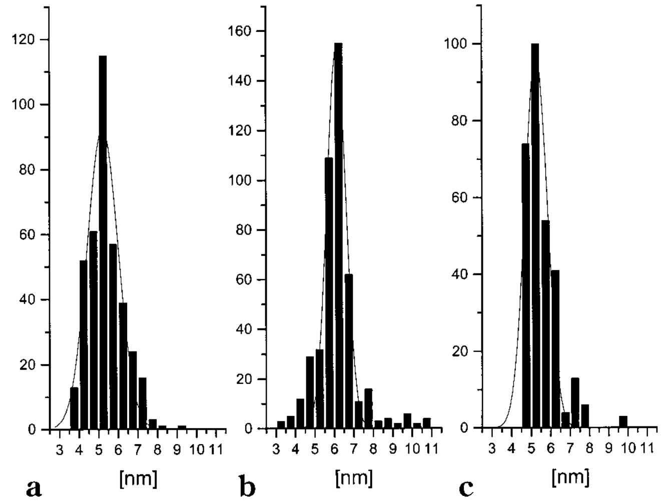


Figure 8. Size distribution of **Td−G$_3$(A$_2$B)(−H)$_{32}$** (a), **Td−G$_4$(A$_2$B)(−H)$_{64}$** (b), and **Biph−G$_4$(A$_2$B)(−H)$_{64}$** (c) derived from electron microscopical data.

The wing of the Gaussian at smaller diameters than the maximum contains fragments or the shape looks pleated in projection. The corresponding sites were encompassed into the statistics as far as they could be recognized. Their number is significant; but since there is no evidence of fragments in the MALDI−TOF experiment, we suggest that the fragments are produced during the preparation of the TEM specimens.

Conclusion and Outlook

The Diels−Alder reaction between an ethynyl-substituted phenylene and a tetraphenylcyclopentadienone derivative allows the simple and rapid synthesis of monodisperse polyphenylene dendrimers up to the fourth generation, with molecular masses higher than 20 000 g/mol.

Polyphenylene dendrimers based on four cores and two types of building units were synthesized. For the dendrimers based on the A$_2$B building unit **1** and the tetraethynylphenylmethane core **4** or the biphenyl core **3**, it could be proven that growth limitations in this case are independent from the core. In contrast, when the A$_4$B building unit **2** is used, the shape of the dendrimer depends less on the core and a globular shape is obtained much faster. However, the shape persistence of these molecules seems to be a result of the very large number of benzene rings within a defined space.

Transmission electron microscopy allows the visualization of the third- and fourth-generation polyphenylene dendrimers. It confirms the diameters obtained by molecular mechanics simulations and gives some impressions about the shape of the dendrimers.

To get further information on polyphenylene dendrimers, light-scattering, SAXS, SANS, and viscosity measurements are currently under way. Apart from those measurements, we are influencing the physical and chemical properties of our dendrimers by suitable derivatization. In principle, this may be done using tetraphenylcyclopentadienones carrying various functional groups during the buildup process or by electrophilic substitution of the final dendrimer. For example, by attaching alkyl chains, self-assembly of the dendrimers on surfaces and in bulk can be observed. Another field of research is the decoration of dendrimers with different numbers of dyes at precise positions on the surface of the molecule and to study their interaction. Furthermore, the dendrimers are being examined for their suitability as, e.g., carriers for catalysts and in the synthesis of peptides.

Experimental Section

General Procedures. All starting materials were obtained from commercial suppliers (Aldrich, Fluka, Fischer, Strem, Acros, Riedel de Haen) and were used without purification. Solvents were used in HPLC grade purity as purchased. All atmosphere-sensitive reactions were performed under argon using Schlenck techniques. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel F-254. Visualization was accomplished with UV light. Flash chromatography was carried out with silica gel 60 (230−400 mesh) from E. Merck. Dry triethylamine was obtained by vacuum transfer from calcium hydride.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500, a Bruker AMX 300, a Bruker Avance 250, or a Varian Gemini 200 spectrometer. Chemical shifts are given in parts per million (ppm), using the solvent signal as reference. The splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants, *J*, are reported in Hertz (Hz). Mass spectral analyses were carried out on ZAB2-SE-FPD (VG Analytical) and Bruker Reflex-TOF spectrometers. MALDI−TOF mass spectra were measured using a 337 nm nitrogen laser and 1,8,9-trihydroxyanthracene as matrix. A gel permeation chromatography (GPC) system equipped with a Waters model 590 pump at a flow rate of 1.0 mL/min and a RI ERC 7512 (ERMA Inc.) differential refractometer were used for molecular weight measurements on SDV-gel columns (particle size 10 mm; porosity 500, 10^4, 10^6 Å) supplied by PSS with toluene as mobile phase. Elemental analyses were obtained on a Foss Heraeus vario EL instrument. Because of the high carbon content in some molecules, the combustion may have been incomplete (sooting) resulting in lower values than expected for the carbon content. Vapor pressure osmometry (VPO) was recorded on a Corona Wescan 232A from Gamma Analyzentechnik GmbH in THF at 30 °C. Thermogravimetrical measurements (TGA) were carried out on a Mettler TG50 instrument in air and differential scanning calorimetry on a Mettler DSC instrument at 10 K/min.

TEM. Specimens for electron microscopical investigation were prepared by spin coating of dilute solutions in dichloromethane (concentrations between 10^{-8} and 10^{-9} mol/L) onto mica substrates and subsequently shadowed in a Balzers 250T high vacuum apparatus with a tungsten tantalum alloy. For shadowing and preparation of a thin carbon supporting film, electron beam evaporators were used. (Due to the restricted size of the vacuum recipient and of both evaporators the shadowing angle was between 30 and 45°.) Shadowing with W/Ta was applied because this alloy is known to have the finest grain of all kinds of metal shadowing.[40] Finally the metal and carbon films containing the dendrimer molecules were floated off the mica substrates onto a water surface and transferred to 600 mesh hexagonal copper grids. To avoid corrosion of the metal film during exposure to the ambient, one grid was inserted immediately after evaporation and floating off into the TEM, and the others were stored in vacuo until they were used. For electron microscopic observation, either a Philips CM 12 or a LEO 912 TEM, was used at a high voltage of 80 kV. Micrographs were recorded either on Ilford PAN F 35 mm photographic film or in digital form by means of a Dage SIT 66 camera adapted to the LEO TEM. Owing to the irregular shape of the dendrimers, we needed a parameter appropriate to characterize the size of the dendrimers. For this purpose, we described a circle about each molecule and assigned its diameter as the apparent size of the dendrimer. For statistical evaluation, between about 250 and 450 particles were measured on micrographs, the diameters of which were the basic data for the histograms. The mean value of the corresponding Gaussians were used as the typical diameter of the dendrimers of the corresponding generation.

Synthesis. The synthesis of 3,3′,5,5′-tetraethynylbiphenyl (**3**),[41] tetrakis(4-ethynylphen-1-yl)methane (**4**),[42] 1,3,5-triethynylbenzene (**5**),[43] 1,2-bis(4-bromphenyl)ethyne (**17**),[44] 4,4′-bis(tri-*iso*-propylsilylethynyl)benzil (**21**),[41] 3,4-bis(4-tri-*iso*-propylsilylethynylphenyl)-2,5-diphenylcyclopenta-2,4-dienone (**1**),[41] **Hex−G$_1$(A$_2$B)(−H)$_{12}$**, and **Tri−G$_1$(A$_2$B)(−H)$_6$**[20] have been reported previously. Also the dendrimers **Biph−G$_1$(A$_2$B)(−EthynylTiPS)$_8$**, **Biph−G$_1$(A$_2$B)(−Ethynyl)$_8$**, **Biph−G$_2$(A$_2$B)(−EthynylTiPS)$_{16}$**, **Biph−G$_2$(A$_2$B)(−Ethynyl)$_{16}$** and **Biph−G$_3$(A$_2$B)(−EthynylTiPS)$_{32}$** were presented elsewhere.[41]

General Procedure for the Aryl−Ethynyl Coupling to Aromatic Bromo Compounds. The aromatic bromine compound was dissolved in a degassed mixture of two parts of triethylamine and one part of toluene (about 30−40 mL of solvents per gram of bromo compound) under argon. After that, 5 mol % of bis(triphenylphosphine)palladium(II) dichloride and 10 mol % of copper(I) iodide and triphenylphosphine with respect to the bromine on the bromo compound were added under a reversed flow of argon. The flask was then sealed with a septum and the reaction mixture stirred at 50−60 °C for about 10 min, after which 1−1.1 molar equiv of the ethynyl compound (tri-*iso*-propylsilylethyne or trimethylsilylethyne) per bromine on the bromo compound (e.g., 4.0−4.4 mol in the case of **11**) were injected. The reaction mixture was stirred further at 80−90 °C and monitored by TLC until no further conversion could be observed (usually 2−5 h). After allowing the solution to cool, it was poured into an equivalent volume of dichloromethane and filtered. Hydrochloric acid, about 6 M, was carefully added to the filtrate until the aqueous phase became slightly acidic (pH < 5). After that, the organic phase was removed, washed twice with distilled water, extracted with a saturated solution of ammonium chloride, washed again several times with distilled water, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product purified by recrystallization or column chromatography on silica gel.

General Procedure for the Diels−Alder Cycloaddtion of Ethynyl- and Tetraphenylcyclopentadiene Derivatives. A mixture of the ethynyl derivative and 1.5 molar equivalents of tetraphenylcyclopentadienone derivative per ethynyl-bond was refluxed for 10 h in 10 mL of *o*-xylene per gram of the starting materials under an argon atmosphere. The cooled reaction mixture was added dropwise to 100 mL of ethanol. The precipitated product was filtered under suction and re-precipitated several times in ethanol until the red color of the cyclopentadienone disappeared. Finally, the product was dried in vacuo.

General Procedure for the Desilylation of Tri-*iso*-propylsilylethynyl Derivatives. A solution of 2 equiv of ammonium fluoride per TiPS group to be removed and 40 mmol of the trialkylsilyl derivative were dissolved under argon in 100 mL of tetrahydrofuran. To the solution was added 4 mmol of *n*-tetrabutylammonium fluoride dissolved in 10 mL of tetrahydrofuran. The end of the reaction (∼2 h) was determined by TLC (silica gel). The solution was then diluted with 500 mL of dichloromethane and extracted with distilled water. The organic phase was removed, washed with 400 mL of 6 M hydrochloric acid followed by 400 mL of distilled water and dried over magnesium sulfate. The solvents were removed in vacuo, and the crude product was purified by reprecipitation.

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Supporting Information Available: Experimanetal, spectroscopic, and analytical data for the synthesized compounds.

This material is available free of charge via the Internet at http://pubs.acs.org.

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