Size and Shape Variation of Polyphenylene Dendrimers through the Heterogeneous Hydrogenation of Embedded Triple Bonds

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ABSTRACT: Different generation polyphenylene dendrimers possessing eight diphenylacetylene units in the dendritic scaffold between the layers of the first and second generation have been synthesized by using a new *p*-phenylene ethynylene-functionalized tetraphenylcyclopentadienone branching unit. The heterogeneous hydrogenation of the embedded triple bonds in the final dendrimers was successfully performed via heterogeneous catalysis. Moreover a "softening" effect of the dendritic structure in consequence of the hydrogenation is observed, allowing for the first time the investigation of this effect upon size, shape, and intramolecular voids in the case of similar dendrimer pairs. Quartz microbalance studies revealed that upon hydrogenation the capacity in host uptake is decreased allowing the incorporation of a lower number of guest molecules compared to the parent materials.

Introduction

While the first account of the synthetic realization of "cascade" or "starburst" growth by Vögtle and co-workers[1] went by almost unnoticed for several years, the work of Tomalia et al.[2] has actually provided the nucleus for rapidly increasing interest in hyperbranched and dendrimer chemistry.[3] Besides the theoretical and experimental work with respect to the properties of this intriguing molecular architecture, important efforts have been made in the assessment of the applications of dendrimers as drug[4] and contrast agent carriers,[5] gene transfer agents,[6] or nanosized carries in combinatorial synthesis.[7] The latter studies were directed at the possible rational design of molecular cavities with tailored properties. This concept was based on a rigid-shell model, assuming an exponentially increasing steric crowding of arms which emanate radially from the core. Shortly after Maciejewski's first explicit mention of possible dense-shell guest inclusion[8] and even before the first publication of Tomalia's synthetic breakthrough,[2] de Gennes and Hervet[9] established a self-consistent field model of starburst growth. This work provided the basis for the dense-shell picture of dendrimers. While dendrimers may well be able to form cavities and accommodate molecular guests within the branched structure after attachment of a rigid shell of a different chemical nature (known as "dendritic box"[10] effect), the open core dense-shell notion stated by de Gennes and Hervet was actually never verified, neither in any subsequent theoretical nor in experimental work. Moreover, theoretical[11] and experimental[12] studies have demonstrated that flexible dendrimers exhibit maximum density in the core of the molecule ("dense-core model") and that there is a finite probability for the end groups to be located at any position within the molecule.

So far, most work was devoted to dendrimers with arms made up of flexible units. However, dendrimers with rather rigid arms, incapable of considerable back folding, may actually be expected to comply with the notion of increasing the surface density of arms. Such dendrimers, solely built from phenyl acetylene or phenylene units, were introduced earlier by Moore et al.[13] and Miller et al.[14]

Polyphenylene dendrimers made by iterative Diels−Alder reaction steps of terminal ethynyl groups and functionalized tetraphenylclyclopentadienones were recently introduced and further developed by our group.[15,16] The structural feature of strongly interlocked pentaphenylbenzene branching points in these new structures suggests high stiffness and shape persistence. Indeed, considerable rigidity and shape persistence of these molecules were suggested by molecular dynamics simulations[17] and verified by atomic force measurements[18] and solid-state NMR investigations.[19] Moreover, experimental studies by small-angle neutron scattering[20] are in accordance with the above results and demonstrate that a fourth generation polyphenylene dendrimer exhibits a molecular structure that can be described by the dense-shell model. This aspect points to a limitation with regard to synthesis; in the past the preparation of polyphenylene dendrimers around a tetraphenylmethane core has been limited to the fourth generation,[21] seemingly because of incomplete conversion at higher generations due the result of steric crowding at the chain ends. Recently, we could overcome this limitation by a size modulation approach through the employment of branching units decorated with terphenyl spacers. In this manner, increased space at the interior of the molecule and decreased steric crowding at the chain ends were induced simultaneously. As a consequence, the synthesis of monodisperse polyphenylene nanoparticles[22] up to a diameter of 22 nm could be accomplished.

In this work, we report a new approach toward extending the diameter of polyphenylene nanoparticles via the introduction of diphenylacetylene units into the dendritic scaffold between the layers of the first and second generation. The heterogeneous hydrogenation of the embedded triple bonds is probed in order to permit a direct assessment of the shielding effect of the outer polyphenylene shell. Moreover, a softening effect of the dendritic structure in consequence of the hydrogenation is expected, allowing for the first time the investigation of this

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effect upon size, shape, and intramolecular voids in the case of similar dendrimer pairs.

Experimental Section

Materials and Instruments. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX250, AC300, AMX500, and AMX700 NMR spectrometers using the residual proton of the solvent or the carbon signal of the deuterated solvent as an internal standard. Field desorption mass spectra (FDMS) were performed with a VG-Instruments ZAB 2-SE-FDP using 8 kV as accelerating voltage. MALDI-TOF mass spectra were measured using a Bruker Reflex II, which was calibrated against poly(ethylene glycol) (3000 g/mol). Samples for MALDI-TOF MS were prepared by mixing the analyte with the matrix (dithranol) in THF in a ratio of 1:250. In some cases, cationization by mixing the matrix with potassium trifluoroacetate (K) or silver trifluoroacetate (Ag) was performed. All reported MALDI-TOF MS measurements were within the experimental error, characteristic for the applied technique. UV−vis absorbance spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of the Johannes Gutenberg University, Mainz. Elemental analyses were performed on all solids except for the dendrimers. The porosity of the dendrimers incorporating small quantities of solvent impurities as well as the incomplete combustion limit the effectiveness of elemental analyses for polyphenylene dendrimer samples. The results obtained from the elemental analyses of the dendrimers differed significantly from the expected values. As such, the MALDI-TOF results in combination with ^{1}H NMR were relied upon more heavily for the identification of the samples. Melting points were measured using a Büchi melting point apparatus B545. Size exclusion chromatography (SEC) was performed in THF at room temperature using a 515 pump (Waters), 717plus injector (Waters), 10 μm guard column, SDV GPC columns with 500, 104, and 106 Å porosities (PSS, Mainz), and UV S-3702 (SOMA) (at 254 nm) and RI ERC 7512 refractive index (ERMA Inc.) detectors. SEC data analysis was performed using WinGPC (PSS, Mainz). Molecular mechanics calculations were performed with PC Spartan Pro (Wavefunction, Inc.). Quartz microbalance (QMB) measurements were performed with the equipment as described previously.[42−43]

Compounds **2**,[28] **6**,[40] **8**,[21] and **13**[15] were synthesized analogous to the literature and were identified by ^{1}H NMR spectroscopy and FD mass spectrometry. Compound **1** and cyclopentadienone **11** were purchased from Aldrich and were used as received. All reactions were performed under a blanket of argon. Dichloromethane was dried by distillation from P_2O_5. CCl_4 was dried over 4 Å molecular sieves. All other materials were used as received from Aldrich.

Compound 3. In a 1L flask, a mixture of water (30 mL), acetic acid (300 mL), concd sulfuric acid (9 mL), CCl_4 (60 mL), iodine (13.2 g, 52.0 mmol), periodic acid (5.93 g, 26 mmol), and 1,4-di-*n*-butylbenzene (10 g, 52 mmol) was heated to reflux overnight. After the mixture was cooled to room temperature, it was poured into water and extracted with hexane. The combined organic layers were subsequently washed with 1 N Na_2CO_3 and 1 N $Na_2S_2O_3$ and then dried over $MgSO_4$. The solvent was removed under reduced pressure and **3** was isolated by column chromatography using hexane as the eluent (R_F = 0.73). After the evaporation of the solvent, the material was recrystallized from EtOH to give a colorless solid (18.94 g, 81%). Mp: 47.2−47.4 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K, δ): 7.63 (s, 2H$_{Ar}$), 2.64, 2.62, 2.58 (t, 4 H, 2 × CH_2), 1.59−1.32 (m, 8 H, overlap of 2 × CH_2), 0.98, 0.95, 0.92 (t, 6 H, 2 × CH_3) ppm. ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300°K, δ): 145.27, 139.71, 100.60, 39.84, 32.73, 22.76, and 14.07 ppm. FDMS *m*/*z*: 442.2 (100%), [M$^+$], (calcd 442.12). Elemental analysis calcd for $C_{14}H_{20}I_2$: C, 38.03; H, 4.56. Found: C, 38.01; H, 4.45.

Compound 4. To a degassed solution of 2,5-dibutyl-1,4-diiodobenzene (6.34 g, 14.30 mmol) in dry THF (50 mL), piperidine (10 mL), 1-bromo-4-ethynyl-benzene (1.73 g, 9.56 mmol) at 0 °C were added consecutively CuI (54 mg, 0.29 mmol) and $Pd(PPh_3)_2Cl_2$ (100 mg, 0.14 mmol). The reaction mixture was stirred overnight at room temperature, and then CH_2Cl_2 and water were added to it. The two phases were separated, and the organic layer was washed with NH_4Cl (aq), cold 1 N HCl, 10% $NaHCO_3$ (aq) and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the crude material was purified by means of column chromatography using hexane as the eluent (R_F = 0.44). Upon evaporation of the solvent, a colorless oil, which slowly solidified, was obtained (2.07 g, 44%). Mp: 46.5−47.5 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K, δ): 7.71 (s, 1H$_{Ar}$), 7.51 (d, 2H$_{Ar}$, ^3J = 8.53 Hz), 7.40 (d, 2H$_{Ar}$, ^3J = 8.21 Hz), 7.32 (s, 1H$_{Ar}$), 2.78−2.64 (m, 4H, 2 × CH_2), 1.69−1.36 (m, 8H, 2 × CH_2), and 1.00−0.93 (m, 6H, 2 × CH_3) ppm. ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K, δ): 144.49, 143.26, 139.96, 133.20, 132.56, 132.06, 122.83, 122.74, 122.70, 101.52, 92.66, 89.22, 40.21, 33.81, 33.19, 32.73, 22.95, 22.80, and 14.14 ppm. FDMS *m*/*z*: 494.8 (100%), 496.8 (100%) [M$^+$], (calcd: 495.26, 497.26). Elemental analysis calcd for $C_{22}H_{24}BrI$: C, 53.36; H, 4.88. Found: C, 53.29; H, 4.82.

Compound 5. To an ice bath cooled mixture of **4** (2 g, 4 mmol), CuI (0.03 g, 0.18 mmol), and $PdCl_2(PPh_3)_2$ (0.06 g, 0.09 mmol) in dry THF (30 mL) and Et_3N (10 mL), triisopropylsilylacetylene (1 mL, 4.4 mmol) was added dropwise. The reaction was stirred at room temperature for 15 h, and then CH_2Cl_2 and water were added to it till phase separation was observed. The two phases were separated, and the organic layer was washed with NH_4Cl (aq), cold 1 N HCl, 10% $NaHCO_3$ (aq) and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the crude material was purified by means of column chromatography using hexane as the eluent (R_F = 0.49) to give a yellowish oil (2.13 g, 95.5%). ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K, δ): 7.53 (d, 2H$_{Ar}$, ^3J = 8.53 Hz), 7.39 (d, 2H$_{Ar}$, ^3J = 8.53 Hz), 7.33, 7.32 (2 s, 2H$_{Ar}$), 2.80−2.74 (t, 4H, CH_2), 1.70−1.56 (m, 4H, CH_2), 1.46−1.34 (m, 4H, CH_2), 1.15 (s, 21H, *i*-Pr_3Si), and 0.98−0.91 (m, 6H, CH_3) ppm. ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K, δ): 143.07, 142.65, 133.28, 133.23, 132.61, 132.17, 123.48, 122.81, 122.77, 122.54, 105.89, 95.95, 93.00, 89.81, 34.41, 34.14, 33.35, 23.08, 23.04, 18.85, 14.16, and 11.76 ppm. FDMS *m*/*z*: 551.1 (100%), 553.0 (100%), [M$^+$], (calcd for $C_{33}H_{45}BrSi$: 549.72, 551.72).

Compound 7. A mixture of **6** (540 mg, 0.85 mmol) and **5** (1.23 g, 2.20 mmol) were dissolved in toluene (15 mL) and combined with a solution of K_2CO_3 (0.47 g, 3.40 mmol) in water (10 mL) in a 100 mL Schlenk flask. The reaction mixture was degassed and flushed with argon, and $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol) was added to it under continuous argon flow. After the reaction mixture was refluxed overnight, it was cooled to room temperature and the two phases were separated. The aqueous phase was extracted twice with CH_2Cl_2, and the organic phases were combined and dried over $MgSO_4$. After solvent evaporation under reduced pressure, the product was purified by means of silica column chromatography using PE/CH_2Cl_2 as the eluent (first 3:1 to remove the starting material and then 2.5:1 to collect the product, TLC (1:1.5 PE:CH_2Cl_2), R_F = 0.36) to give a reddish yellow powder (0.37 g, 33%). T_{dec} > 250 °C. ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 273 K, δ): 7.56−7.51 (m, 8H$_{Ar}$), 7.43 (d, 4H$_{Ar}$, ^3J = 8.12 Hz), 7.28−7.23 (m, 14H$_{Ar}$), 6.99 (d, 4H$_{Ar}$, ^3J = 8.13 Hz), 2.73−2.68 (m, 8H, CH_2), 1.62−1.54 (m, 8H, CH_2), 1.39−1.31 (m, 8H, CH_2), 1.08 (s, 42H, *i*-Pr_3Si), and 0.91−0.86 (m, 12H, CH_3) ppm. ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 273 K, δ): 200.72, 154.22, 142.96, 142.44, 140.21, 139.97, 133.21, 132.50, 132.44, 132.28, 131.00, 130.49, 130.44, 128.52, 127.94, 127.13, 126.63, 125.89, 123.27, 123.07, 122.67, 105.79, 95.96, 94.04, 89.94, 34.43, 34.20, 33.24, 23.10, 19.05, 14.42, 14.38, and 11.66 ppm. FDMS *m*/*z*: 1324 (100%), [M$^+$], (calcd 1322.09). Elemental analysis calcd for $C_{95}H_{108}OSi_2$: C, 86.31; H, 8.23. Found: C, 86.28; H, 8.44.

Dendrimer 9. A mixture of **8** (20 mg, 0.048 mmol) and **7** (305 mg, 0.230 mmol) in *o*-xylene (5 mL) was refluxed for 24 h under argon. After cooling to room temperature the solvent was removed in vacuo. The residue was purified by means of column chromatography using PE/CH_2Cl_2 (2.5/1) to give a colorless solid (178 mg, 66%). T_{dec} > 250 °C. ^{1}H NMR (700 MHz, $C_2D_4Cl_4$, 393 K, δ): 7.58 (s, 4H$_{Ar}$), 7.44−7.39 (m, 30H$_{Ar}$), 7.27−7.11 (m, 52H$_{Ar}$),

6.97−6.74 (m, 54H_{Ar}), 2.76 (m, 32H, CH_2), 1.65 (m, 32H, CH_2), 1.39 (m, 32H, CH_2), 1.15 (s, 168H, TIPS), and 0.92 (m, 48H, CH_3) ppm. ^{13}C NMR (175 MHz, $C_2D_4Cl_4$, 273 K, δ): 144.68, 142.92, 142.39, 141.95, 141.20, 141.11, 140.86, 140.75, 140.69, 140.35, 140.18, 139.98, 139.84, 139.52, 138.81, 136.99, 136.71, 133.18, 132.44, 132.06, 132.04, 131.38, 130.68, 130.34, 129.01, 128.02, 127.19, 126.97, 126.61, 125.68, 125.40, 123.13, 122.80, 123.13, 122.24, 105.84, 95.84, 94.21, 89.45, 34.42, 34.19, 33.22, 23.09, 19.05, 14.40, 14.37, and 11.66 ppm. MALDI-TOF (dithranol): exact mass calcd for $[M + Ag]^+$ $C_{409}H_{452}Si_8Ag$, 5 700.85; found, 5 700.

Dendrimer 10. To a mixture of **9** (177 mg, 0.032 mmol) in THF (8 mL), tetrabutylammonium fluoride trihydrate (88 mg, 0.27 mmol) in THF (2 mL) was added. The reaction mixture was stirred at room temperature for 30 min. After the mixture was quenched with H_2O, it was concentrated in vacuo, and the residue was poured into a methanol/water mixture (4/1). The precipitated product was collected by filtration and was dried in vacuo to yield a colorless solid (116 mg, 85%). ^{1}H NMR (500 MHz, CD_2Cl_2, 273 K, δ): 7.62 (s, 4H_{Ar}), 7.50−7.46 (30H_{Ar}), 7.34−7.16 (m, 52H_{Ar}), 7.03−6.72 (m, 54H_{Ar}), 3.27, 3.35 (2 s, 8H, acetylene H), 2.80−2.73 (m, 32H, CH_2), 1.68−1.58 (m, 32H, CH_2), 1.42−1.36 (m, 32H, CH_2), and 0.96−0.92 (m, 48H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 273 K, δ): 145.22, 145.14, 143.37, 142.74, 142.36, 141.73, 141.70, 141.59, 141.54, 140.98, 140.74, 140.68, 140.38, 140.34, 140.10, 139.44, 137.80, 137.73, 137.55, 133.56, 132.74, 132.25, 131.60, 130.90, 130.53, 129.33, 128.23, 127.43, 127.12, 126.94, 126.21, 125.88, 125.61, 123.72, 122.66, 122.62, 122.07, 94.49, 89.35, 82.87, 81.91, 34.20, 33.97, 33.28, 33.19, 23.05, 22.97, 14.20, and 14.13 ppm. MALDI-TOF (dithranol): exact mass calcd for $[M + H^+]^+$ $C_{337}H_{292}$, 4 342.08; found, 4 344.

Dendrimer 12. A mixture of **10** (50 mg, 0.012 mmol) and **11** (45 mg, 0.12 mmol) in *o*-xylene was heated at 130 °C for 3 days. After the mixture was cooled to room temperature, the solvent was removed in vacuo. The residue was purified by means of column chromatography using PE/CH_2Cl_2 (1/1) to give a colorless solid (50 mg, 63%). T_{dec} > 216 °C. ^{1}H NMR (700 MHz, $C_2D_4Cl_4$, 370 K, δ): 7.58 (s, 4H_{Ar}), 7.43−7.34 (m, 38H_{Ar}), 7.21−6.72 (m, 266H_{Ar}), 2.76, 2.58, 2.44, 2.35 (4 s, br, 32H), 1.50 (m, 32H, CH_2), 1.28−1.23 (m, 32H, CH_2), and 0.88−0.83 (m, 48H, CH_3) ppm. ^{13}C NMR (175 MHz, $C_2D_4Cl_4$, 370 K, δ): 144.97, 142.21, 142.12, 141.92, 141.74, 141.36, 141.20, 141.05, 140.72, 140.64, 140.58, 140.43, 140.36, 140.12, 140.08, 139.99, 139.61, 139.04, 138.13, 137.48, 137.24, 132.40, 131.94, 131.89, 131.84, 131.36, 131.16, 130.61, 130.18, 129.01, 127.66, 126.96, 126.76, 126.67, 126.28, 125.67, 125.36, 122.86, 122.80, 121.18, 92.55, 90.12, 33.91, 33.01, 32.93, 32.63, 22.86, 22.50, 14.12, and 13.95. UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 321 nm (453 916 mol^{-1} dm^3 cm^{-1}). MALDI-TOF (dithranol): exact mass calcd for $[M+Ag]^+$ $C_{561}H_{452}Ag$, 7 302.86; found, 7 307.

Dendrimer 14. A solution of **10** (40 mg, 0.0092 mmol) and **13** (0.13 g, 0.11 mmol) in Ph_2O (3 mL) was heated at 185 °C for 3 days. After the reaction mixture was cooled to room temperature, the solution was poured into acetone, and the precipitated product was collected by filtration, washed with acetone and methanol, and dried in vacuo to yield a colorless solid (94 mg, 75%). T_{dec} > 280 °C. ^{1}H NMR (700 MHz, $C_2D_4Cl_4$, 370 K, δ): 7.57 (s, 4H, Ar), 7.40−6.50 (m, 624H, Ar), 2.75, 2.57, 2.39, 2.29 (4 s, br, 32H, CH_2), 1.48 (s, br, 32H, CH_2), 1.24 (s, br, 32H, CH_2), and 0.87−0.80 (m, 48H, CH_3) ppm. ^{13}C NMR (175 MHz, $C_2D_4Cl_4$, 370 K, δ): 144.94, 142.28, 142.23, 142.07, 142.05, 141.80, 141.46, 141.31, 140.85, 140.78, 140.62, 140.43, 140.39 140.31, 140.12, 140.07, 139.99, 39.53, 139.48, 139.43, 139.37, 139.19, 139.06, 138.74, 138.59, 138.32, 138,26, 138.09, 131.82, 131.27, 131.22, 130.23, 130.20, 128.85, 128.57, 127.67, 126.93, 126.78, 126.62, 126.29, 125.58, 125.30, 122.84, 121.11, 92.53, 90.14, 33.88, 32.93, 32.54, 22.82, 22.48, 14.13, and 13.98 ppm. UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 251 (800 681) and 315 nm (520 769 mol^{-1} dm^3 cm^{-1}). MALDI-TOF (dithranol): exact mass calcd for $[M+K]^+$ $C_{1041}H_{772}K$, 13 320.76; found, 13 319 and exact mass calcd for 2 × $[M + K]^+$ dimer of $C_{1041}H_{772}$, 26 550; found, 26587.

Hydrogenated Dendrimer 15. To a solution of **12** (38 mg, 0.0052 mmol) in $CHCl_3$ (4 mL), palladium on carbon (10% Pd/C, 4 mg) was added. The reaction mixture was saturated with H_2 for 15 min and was stirred at 50 °C under hydrogen atmosphere for 1 week. The reaction mixture was then passed through a silica bead to separate the product from the catalyst. Upon evaporation of the solvent, a colorless solid was obtained (35 mg, 92%). ^{1}H NMR (700 MHz, $C_2D_4Cl_4$, 370 K, δ): 7.58 (s, 4H_{Ar}), 7.40−6.71 (m, 304H, Ar), 2.77 (s, 32H, CH_2 of CH_2-CH_2), 2.44, 2.40, 2.31 (3 s, br, 32H, CH_2), 1.36−1.22 (m, 64H), and 0.88−0.76 (m, 48H, CH_3). ^{13}C NMR (175 MHz, $C_2D_4Cl_4$, 370 K, δ): 144.93, 142.40, 142.27, 141.72, 141.55, 141.23, 141.16, 141.05, 140.97, 140.73, 140.61, 140.45, 140.28, 140.14, 140.02, 139.67, 139.33, 139.23, 139.17, 138.83, 138.56, 138.50, 138.10, 137.84, 137.69, 137.66, 136.78, 132.27, 132.21, 131.95, 131.90, 131.50, 130.60, 130.22, 129.69, 129.48, 129.18, 128.99, 128.94, 128.76, 128.37, 127.77, 127.60, 127.41, 126.93, 126.81, 126.74, 126.63, 126.55, 126.41, 126.18, 125.93, 125.70, 125.55, 125.40, 125.27, 125.13, 37.32 (CH_2CH_2), 34.78 (CH_2CH_2), 33.46, 33.10, 32.77, 31.92, 22.86, 22.75, 14.14, and 14.00 ppm. UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 260 nm (551 596 mol^{-1} dm^3 cm^{-1}); MALDI-TOF (dithranol): exact mass calcd for $[M + K]^+$ $C_{561}H_{484}K$, 7265.11; found, 7263.

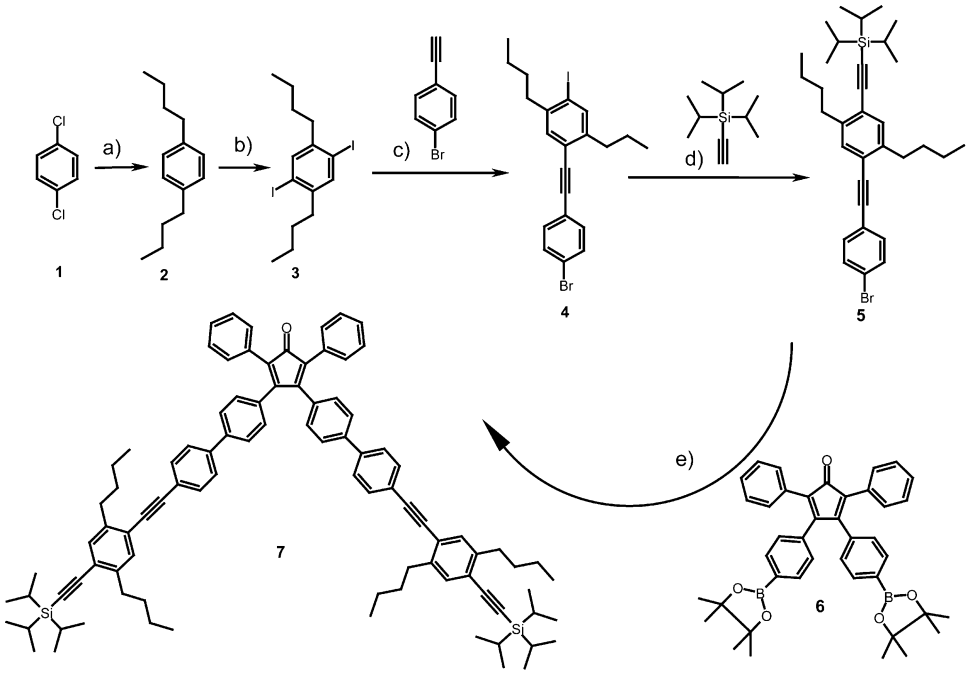
Hydrogenated Dendrimer 16. Palladium on carbon (10% Pd/C, 33 mg) was suspended in a degassed solution of **14** (70 mg, 0.0052 mmol) in 5 mL o-xylene. The reaction mixture was saturated with H_2 for 15 min stirred at 136 °C under hydrogen atmosphere for one week. After the reaction mixture was cooled to room temperature, the crude material was passed through a silica bead to separate the product from catalyst. Evaporation of the solvent produced dendrimer **16** in the form of a colorless solid (60 mg, 86%). ^{1}H NMR ($C_2D_4Cl_4$, 700 MHz, 370 K, δ): 7.56 (s, 4H, Ar), 7.40−6.50 (m, 624H, Ar), 2.74 (s, 32H, CH_2 of CH_2-CH_2), 2.44, 2.40, 2.30 (m, 32H, CH_2), 1.41−1.19 (m, 64H, 2 × CH_2), and 0.86−0.75 (m, 48H, CH_3) ppm. ^{13}C NMR (175 MHz, $C_2D_4Cl_4$, 370 K, δ): 144.94, 142.41, 142.29, 142.07, 142.04, 141.55, 141.27, 141.05. 140.85, 140.81, 140.76, 140.69, 140.67, 140.46, 140.40, 140.34, 140.27, 140.18, 139.90, 139.69, 139.52, 139.45, 139.38, 139.26, 138.98, 138.88, 138.85, 138.76, 138.64, 138.58, 138.50, 138.45, 138.09, 137.81, 137.72, 137.68, 136.71, 136.59, 132.25, 131.82, 131.58, 131.32, 130.60, 130.24, 130.19, 129.88, 129.35, 129.26, 128.92, 128.82, 128.53, 127.76, 127.64, 126.91, 126.62, 126.55, 126.26, 126.19, 126.04, 125.63, 125.57, 125.43, 125.30, 125.12, 37.40, 37.36, 34.55, 34.51, 33.43, 33.05, 33.03, 32.70, 31.90, 22.81, 22.72, 14.12, and 13.99 ppm. UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 258 nm (910 565 mol^{-1} dm^3 cm^{-1}). MALDI-TOF (dithranol): exact mass calcd for $[M + K]^+$ $C_{1041}H_{804}K$, 13352.76; found, 13349.

Results and Discussion

Synthetic Strategy. The synthesis of polyphenylene dendrimers is possible in both divergent[21] and convergent[15] manner. Both synthetic approaches are based on the Diels−Alder cycloaddition between core building blocks bearing multiple alkyne moieties and the diene unit of a substituted cyclopentadienone.[23] In addition, the triisopropylsilyl (T*i*PS) protecting group strategy permits the employment of the above cycloaddition reaction in a selective way, thus rendering it an optimal synthetic tool for dendrimer synthesis.

In the present case, a new tetraphenylcyclopentadienone building block was needed that would permit a divergent synthesis based upon Diels−Alder cycloaddition and T*i*PS deprotection steps as well as the embedding of (−C≡C−) moieties into the scaffold of the final dendrimers. The tetraphenylcyclopentadienone derivative **7** carrying *p*-phenylene ethynylene units and terminal T*i*PS protected ethynyl groups, as presented in Scheme 1, was expected to fulfill the above demands. The compound **7** contains two pairs of inequivalent −C≡C− triple bonds, one of which being subjected to deprotection during the reaction sequence of the divergent

Scheme 1. Synthesis of Branching Unit 7[a]



[a] Key: (a) Et_2O, *n*-BuMgBr, dichlorobis(triphenylphosphine)nickel(II), 84.5%; (b) CCl_4, CH_3COOH, H_2SO_4, I_2, H_5IO_6, 81%; (c) THF, piperidine, room temp, CuI, $Pd(PPh_3)_2Cl_2$, 44%; (d) THF, Et_3N, 0 °C, CuI, $Pd(PPh_3)_2Cl_2$, 95.5%; (e) K_2CO_3, $Pd(PPh_3)_4$, toluene, water, reflux, 33%.

synthesis. Therefore, in order to avoid the emergence of undesired hyperbranched side products, the chemoselectivity of the Diels−Alder step had to be ascertained. It is documented that diphenylacetylene derivatives undergo Diels−Alder cycloaddition reactions with tetraphenylcyclopentadienones at substantially higher temperatures than the terminal alkynes.[23,24] As such the above presented strategy was promising.

Synthesis. The synthesis of **7** was carried out as depicted in Scheme 1. Recently, we have shown that the boronic acid-functionalized tetraphenylcyclopentadienone **6** is a versatile building block, because bromo- or iodo-substituted aromatic compounds with the desired functionality could easily be introduced.[25] Therefore, the asymmetric diphenylacetylene derivative **5** with butyl substituents as solubilizing groups was synthesized, in which the bromo function was designed for the final coupling with **6**.

1,4-Dibutyl-2,5diiodobenzene (**3**) was obtained readily in a two-step procedure consisting of a Grignard reaction and a subsequent iodination.[26] The following Hagihara−Sonogashira[27] cross-coupling with 1 equiv of *p*-bromophenylacetylene produced the diphenylacetylene derivative **4** in moderate (44%) yield. The different substitution pattern at the two ends of **4** assured that the second Hagihara−Sonogashira cross-coupling with triisopropylsilylethyne could be carried out selectively on the iodo function to obtain **5** in high yield. Unfortunately, the Suzuki cross-coupling[28] of **5** with **6** gave the desired diphenylacetylene substituted tetraphenylcyclopentadienone in moderate yield (33%), even when different catalyst/base and solvent systems were employed.

As pointed out above, the key step in the synthesis of structurally well-defined polyphenylene dendrimers is the iterative [4 + 2] cycloaddition of the branching unit to an ethynyl-substituted core or dendrimer and the subsequent deprotection of the triisopropylsilyl (T*i*PS) protected ethynyl groups, which activates the molecule for further growth. To introduce the diphenylacetylene groups in the inner dendritic scaffold, **7** was used in the first Diels−Alder step with the core **8** to give the first-generation dendrimer **9** (Scheme 2).

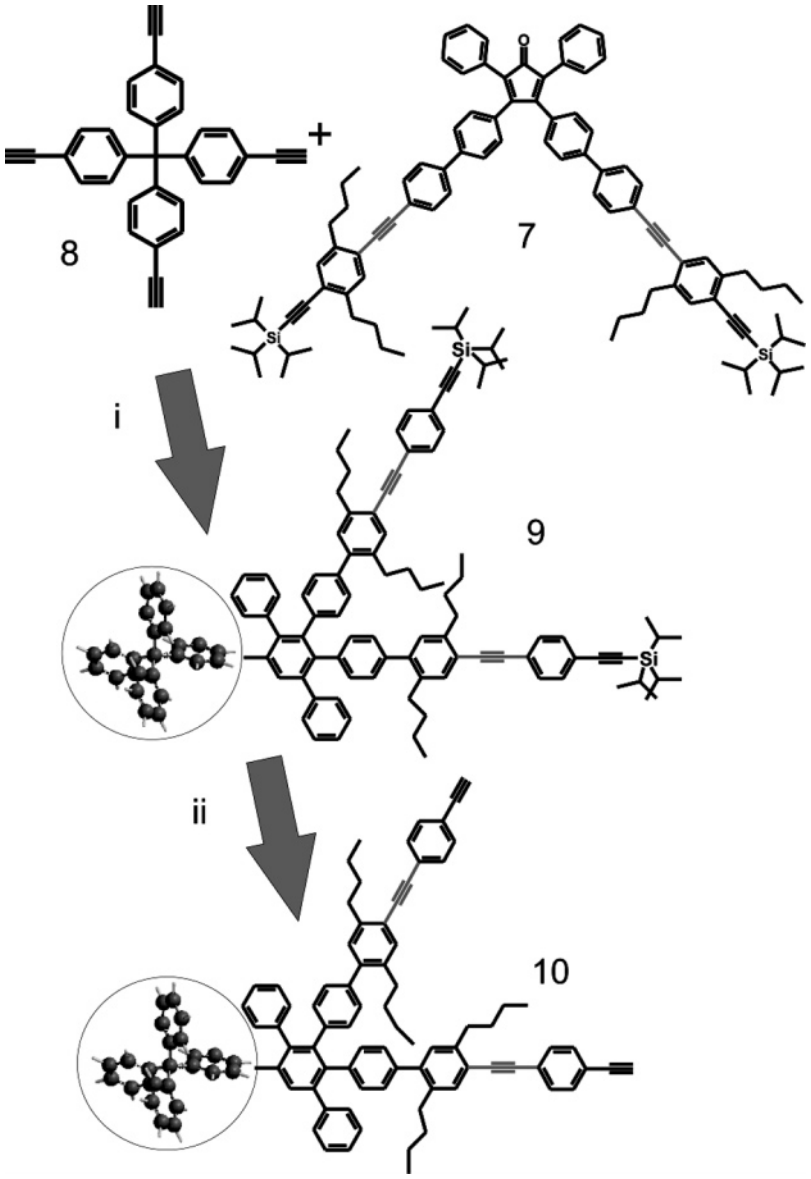
MALDI-TOF mass spectrometry showed that along with the expected product (**9**) small amounts of a side product through the overreaction of one diphenylacetylene unit was also formed. However, via the careful control of the amount of **7** (1.06−1.08 equiv of ethynyl group) during the cycloaddition reaction and by extensive column chromatography, polyphenylene dendrimer **9** having eight T*i*PS-protected 1,4-dibutyl-2-ethynyl-5-phenylethynyl benzene groups at the periphery was produced in 66% yield. Subsequent NMR, MALDI-TOF, and SEC investigations confirmed the purity and monodispersity of compound **9**.

In the following, the quantitative desiylilation of the T*i*PS protecting groups with tetrabutylammonium fluoride led to the ethynyl-functionalized first-generation dendrimer **10,** which represented the starting point for the synthesis of second- and third-generation polyphenylene dendrimers (PDs) bearing eight acetylene groups in the scaffold at the level of the first generation. Accordingly, the Diels−Alder reaction of **10** with tetraphenylcyclopentadienone **11** produced the second-generation PD **12** with eight acetylene groups between the generation layers.

For the synthesis of the third-generation dendrimer **14**, a multiple cycloaddition reaction of **10** was undertaken in the presence of the first-generation dendron **13** (Scheme 3). This method is similar to the double-stage[29] synthesis of dendrimers that was first introduced by Frechét et al. Its advantage in the present case lies in the diminution of the possibility of side product formation; the selectivity of the bulky dendron **13** toward terminal ethynyl groups is superior to that of the usual AB_2 building block due to its higher steric demand. In the same time, applying this synthetic concept, the final third-generation dendrimer is achieved in only one cycloaddition step compared to the classical divergent synthesis, which would involve two iterative Diels−Alder reactions. Accordingly, the third-generation PD **14** was produced in good yield (75%) without the detection of overreacted side products.

The herein described dendrimers possess good solubility in common organic solvents (CH_2Cl_2, toluene, or THF), which

Scheme 2. Synthesis of the First-Generation Dendrimers 9 and 10 with Branching Unit 7[a]



[a] Key: (i) *o*-Xylene, reflux, 66%; (ii) tetrabutylammonium fluoride trihydrate, THF, room temp, 85%.

allowed their purification by column chromatography as well as their complete characterization by standard spectroscopic techniques. ^{1}H NMR spectroscopy showed well-separated and clearly assignable signals for some of the aromatic protons as well as for the protons of the ethynyl, butyl, or TIPS groups. The relative intensities of aromatic and aliphatic signals corresponded well with the expected values. An additional proof of the structure could be obtained from the fact that the characteristic signals of the protons of the core and the pentaphenyl units could be well assigned. Moreover, the protons on the pentaphenyl repeating units showed generation-dependent chemical shifts in the ^{1}H NMR spectra.[15]

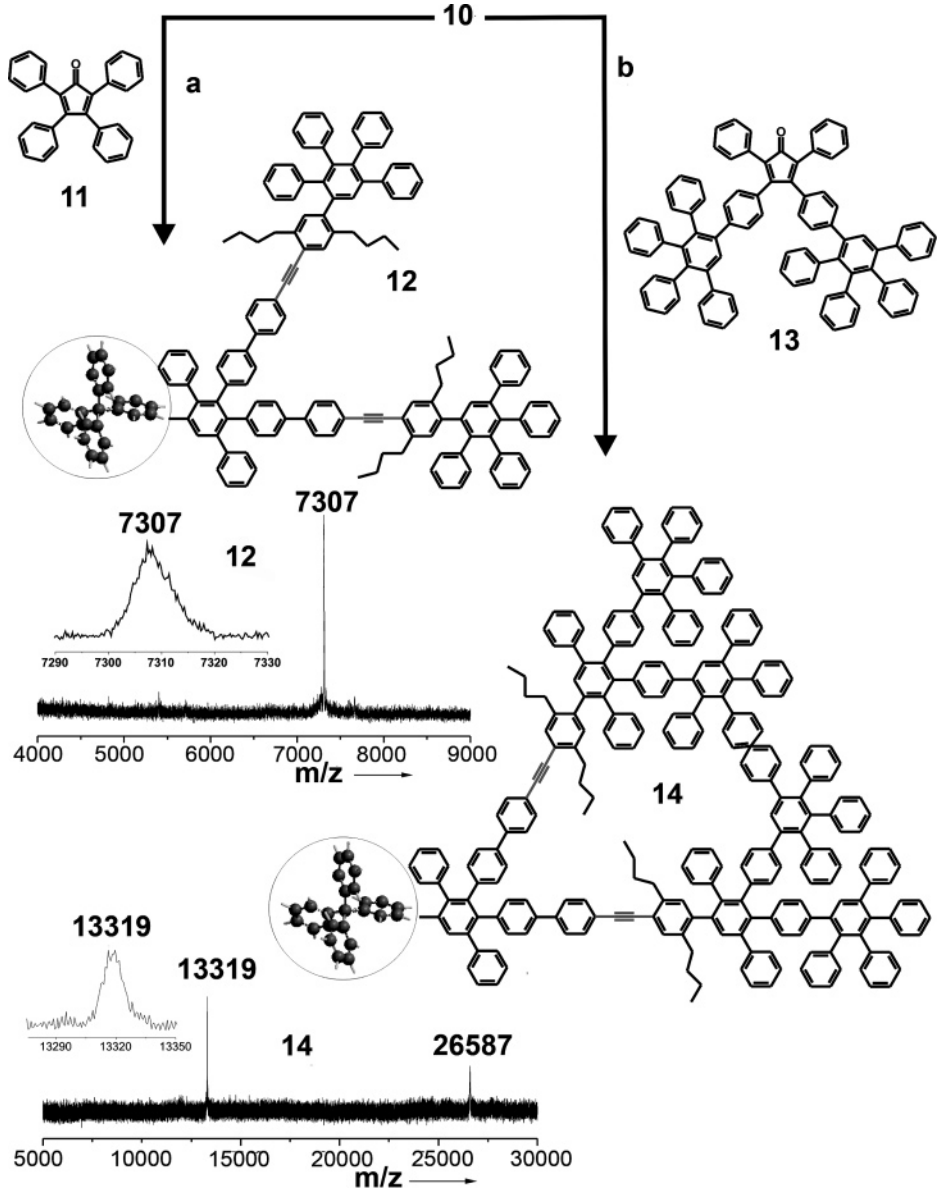
Heterogeneous Hydrogenation. The partial or total hydrogenation of phenylacetylenes, diphenylacetylenes, and polyphenylalkynes in the presence of both homogeneous[32] and heterogeneous[31] catalyst systems is well established. In most of the cases, significant structural changes due to the transition toward structures with a higher number of internal degrees of freedom were documented. From this point of view, the hydrogenation of the diphenylacetylene units in the scaffold of a polyphenylene dendrimer opens up several interesting aspects which are worthwhile to investigate. Beside the question of access of the catalyst to the internal triple bonds, the possible softening of a shape-persistent nanoparticle and the consequences thereof are appealing issues.

To address the possible shielding effect of the polyphenylene shell against the catalyst's diffusion to the acetylene units, both the second- and third-generation dendrimers (**12** and **14**, respectively) were subjects of a heterogeneous hydrogenation process using palladium on carbon (10% Pd/C) as the catalyst system in the presence of hydrogen at atmospheric pressure.

The total hydrogenation of all internal acetylene moieties of **12** proceeded in chloroform at 50 °C during a reaction time of 8 days yielding the dendrimer **15** with eight 1,1′-(1,2-ethanediyl)-bis[benzene] units between the first- and second-generation layers (see Scheme 4). Preliminary reactions conducted at room temperature and shorter reaction times resulted in incomplete hydrogenation.

Compared to the above presented case, **14** showed a decreased tendency toward hydrogenation under similar conditions (1 atm, 50 °C, 10% Pd/C). However, reactions conducted at 136 °C for 8 days in diphenylether eventually produced the total hydrogenation of the internal acetylene units resulting in the third-generation dendrimer **16**.

Scheme 3. Synthesis of the Second- and Third-Generation Dendrimers 12 and 14 Bearing Eight Internal Triple Bonds[a]



[a] Key: (a) *o*-Xylene, 130 °C; 3 days, 70%; (b) Ph_2O, 190 °C, 3 days, 75%. MALDI-TOF spectra for **12** and **14** are also presented.

The indubitable proof of the hydrogenated structures using MALDI-TOF failed since the difference in the molecular mass of the starting compounds (**12** and **14**) and the hydrogenated products (**15** and **16**) of 32 Da is below the width of the observed MW peaks of 20−35 Da, depending upon dendrimer generation and sample preparation method. Yet, ^{1}H and ^{13}C NMR as well as UV−vis and Raman spectroscopy proved to be powerful tools for the evaluation of the degree of hydrogenation.

A comparison between the ^{1}H NMR spectra recorded before and after the hydrogenation shows an interesting feature (Scheme 4). The spectrum of dendrimer **12** prior to hydrogenation shows four well-separated signals for the α protons (Hα) of the dibutylbenzene units at $\delta = 2.76$, 2.58, 2.44, and 2.35 ppm. On investigation of the same area in the spectra of the hydrogenated product **15,** one can see that the difference in their chemical shifts decreases significantly leading to a multiplet centered at $\delta = 2.44$. Moreover, the hydrogenation leads to the appearance of an additional signal ($\delta = 2.77$ ppm) in the benzylic region, which indicates the newly formed 1,2-ethanediyl (Ha) unit in **15.** On the one hand these observations verify the successful hydrogenation of the acetylene moieties, and on the other hand they show that **15** gained an increase in flexibility resulting in changes in the chemical shifts of the Hα signals.

The above observations are also reflected in the ^{13}C NMR spectra of the investigated compounds. Upon hydrogenation, the characteristic signals of the −(C≡C)− units at 92.55 and 90.12 ppm disappear and two new ($-CH_2-$) peaks at 37.32 and 34.48 ppm are recorded.

Additionally, UV−vis and Raman spectroscopy were applied to monitor the reduction of the acetylene moieties. The assessment of the absorption curves before and after hydrogenation reveals major changes in the optical properties of the samples. Before the reduction, the recorded curves of **12** and **14** are dominated by absorption bands at $\lambda_{max} = 259$ and 320 nm. These bands are assigned to the polyphenylene structure and the contained diphenylacetylene units, respectively. The bathochromic shift as compared to the signals of the parent diphenylacetylene[32] ($\lambda_{max} = 298$ nm) can be ascribed to a delocalization over the neighboring phenyl rings of the polyphenylene dendrons. After hydrogenation, the bands at 320 nm disappear in accordance with the disruption of conjugation upon

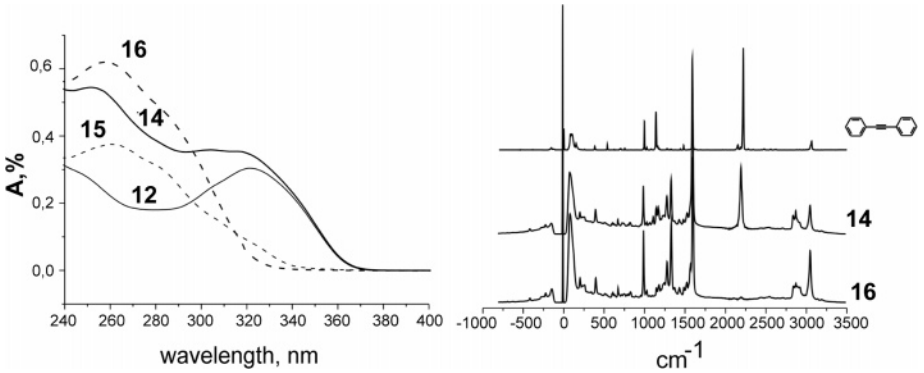
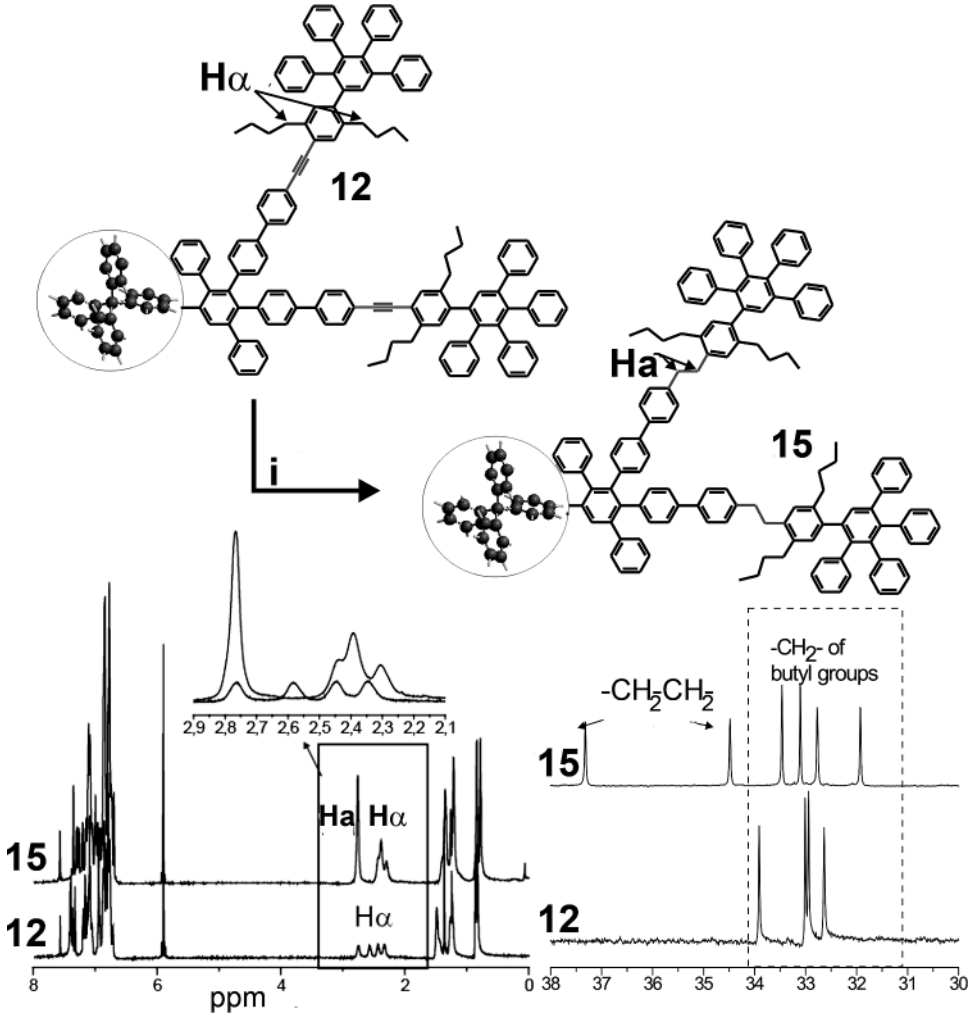


Figure 1. Left: UV−vis spectra of dendrimers **12** and **14** before (solid line) and after (dotted) hydrogenation in dichloromethane, $c = 0.68 \times 10^{-6}$ mg/mmol. Right: Raman spectra of tolane and dendrimer **14** and its hydrogenation product **16**.

Scheme 4. Hydrogenation of the Second-generation Dendrimer 12[a]



[a] $CHCl_3$, H_2, 1 atm, 50 °C, 10% Pd/C, 8 days, 89%.

elimination of the −C≡C− units in the diphenylacetylene chromophores.

Raman spectroscopy is a powerful tool used for the determination and monitoring of the alkyne content in polyphenylacetylenes[33] due to the characteristic vibrational frequency of the −C≡C− triple bond at 2200 cm^{-1}. Thus, the parent diphenylacetylene (tolane), as a model, and the alkyne-containing dendrimers before and after hydrogenation were subjected to Raman spectroscopic investigation. The recorded spectra provide clear information about the presence or absence of −C≡C− triple bonds in these molecules in a fingerprint fashion. In our case (Figure 1), it can be seen that the characteristic frequencies of tolane and the dendrimer **14** amount to 2220 cm^{-1} and 2208 cm^{-1}, respectively. The elimination of the triple bonds in the dendrimer **16** upon reduction was confirmed by the absence of the signal in the region of the alkyne groups.

As pointed out earlier, the structural changes induced by introduction of flexibility into the scaffold of shape-persistent polyphenylene dendrimers raised appealing questions regarding the shape alteration, the self-assembly, and the host−guest properties of these nanoparticles. To assess the hydrogenation-induced changes of the overall shape of the PD, molecular mechanics calculations were carried out by applying the MMFF

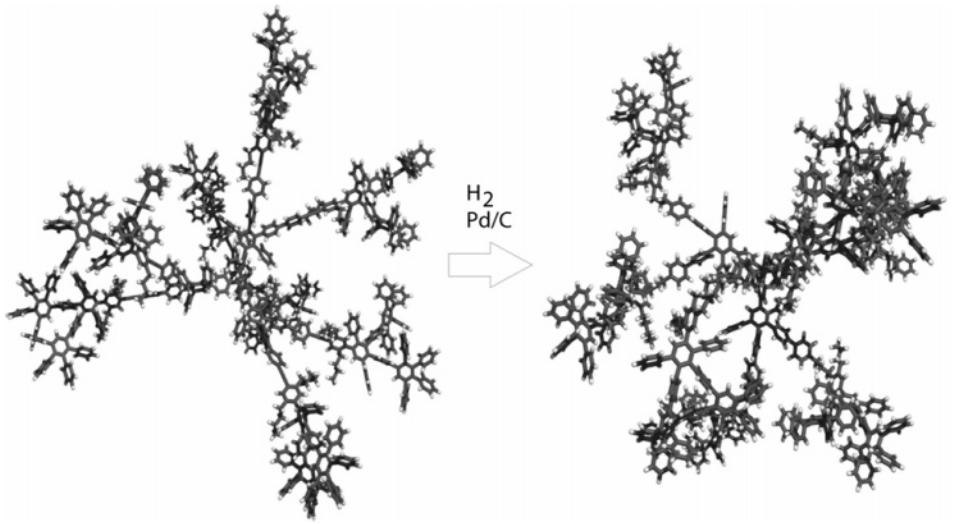


Figure 2. 3D molecular models of dendrimer **14** with stiff 1,2-ethanediyl moieties and its hydrogenated product **16** with flexible 1,2-ethanediyl moieties.

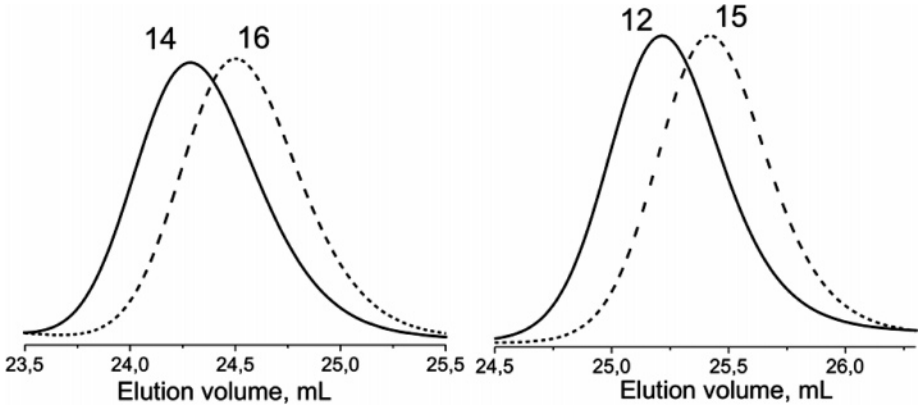


Figure 3. SEC traces for the polyphenylene dendrimers before (**12** and **14**) and after (**15** and **16**) hydrogenation.

Table 1. Frequency Shifts $\Delta\nu$ from QMB Measurements on the Dendrimers 14 and 16 and Comparison of the Number of Coating Molecules and Guest Molecules

analyte	frequency shift, $\Delta\nu$, Hz		N_g (number of guest molecules, units of 10^{12})		N_{cd} (number of coating dendrimer molecules, units of 10^{12})		ratio guest/host (N_g/N_{cd})	
	14	16	14	16	14	16	14	16
aniline, $M = 93.1$	300	90	8536	2561	1990	>1989	4.29	<1.29
benzonitrile, $M = 103.1$	350	120	8993	3084			4.52	<1.55
nitrobenzene, $M = 123.1$	400	180	8608	3870			4.32	<1.95
benzaldehyde, $M = 106.6$	550	300	9072	4950			4.56	<2.49
acetophenone, $M = 120.1$	670	450	14 780	9927			7.43	<5.00

method[36] using the Spartan (by Wavefunction Inc.) program package. Figure 2 shows as an example the three-dimensional structure of the third-generation dendrimer **14** and that of the hydrogenated product **16**. As the unit **7** possesses extended branching arms, the calculated diameter of the final dendrimer **14** (8.2 nm) is significantly larger than that of the corresponding third-generation polyphenylene dendrimer (5.2 nm),[21] produced by the use of the classical branching unit. The three-dimensional molecular model of **14** suggested that even in the scaffold of the third-generation dendrimer the diphenylacetylene units are not completely shielded. As such, the heterogeneous hydrogenation of the inner alkyne groups is possible, though, under harsher conditions than in the case of the second-generation PD **12**. For the case of the hydrogenated product, the 3D model shows a significant decrease of the molecular diameter which amounts to 6.2 nm.

The above structural predictions are supported by the experimental data obtained by size exclusion chromatography (SEC) (Figure 3). Interestingly, the hydrogenation of the acetylene bonds clearly increased the elution volume in both cases investigated (**15** and **16**). This suggests that the hydrogenation of the internal triple bonds causes a sizable decrease in effective volume of the dendrimer, which governs the retention characteristics in the SEC experiments.

It is not immediately clear, however, whether the strong retention of the hydrogenated dendrimers **15** and **6**, compared to the prehydrogenated species **12** and **14**, is caused by an inherently smaller volume of the former or by their flexibility-induced readiness to enter the cavities of the SEC stationary phase.

QMB Measurements. Indirect information on the internal porosity of dendrimers can be obtained from studies of their

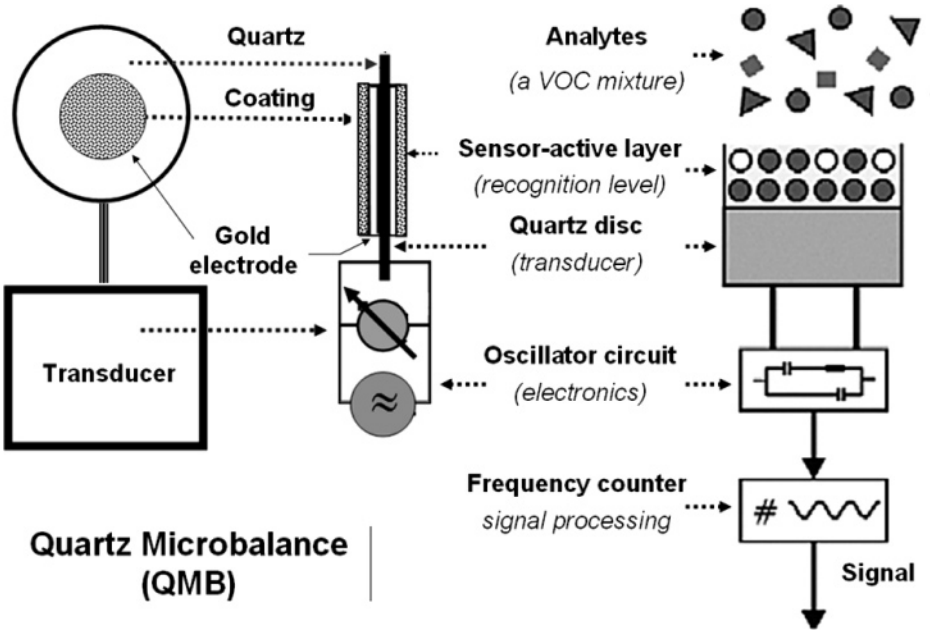


Figure 4. A quartz microbalance (QMB) top coated with a dendrimer as a sensor-active coating serves as an effective detector for volatile organic compounds (VOCs).

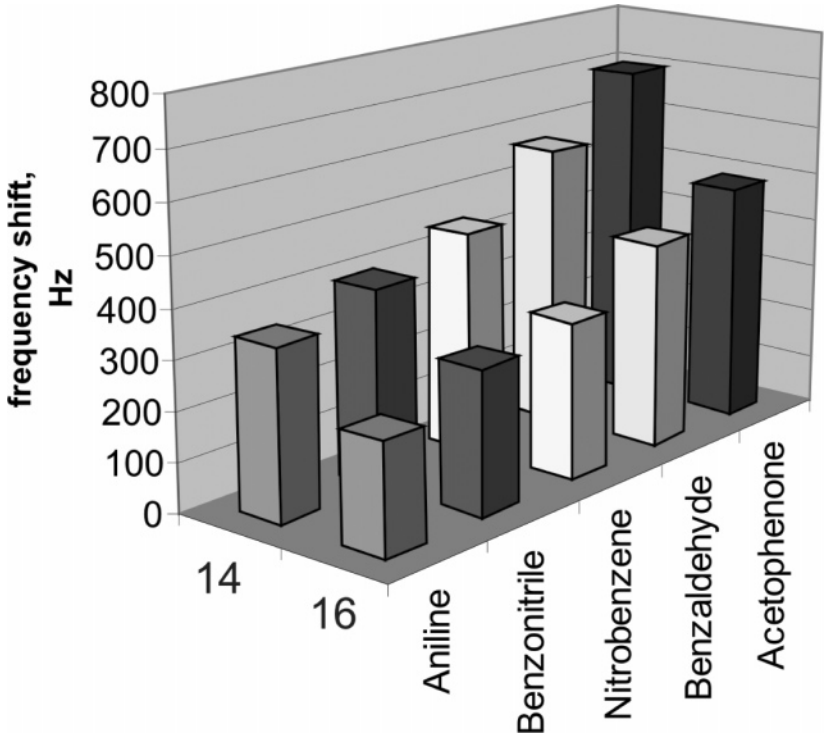


Figure 5. Comparison of the frequency shift $\Delta\nu$ for the pre-hydrogenation dendrimer **14** and the post-hydrogenation dendrimer **16** caused by exposure to various guest molecules.

ability to engage in host−guest interactions. This is of considerable technical relevance as they recommend polyphenylene dendrimers as building blocks for sensors of volatile organic solvents (VOCs).[35] For this purpose, quartz microbalances (QMB) are used, which constitute mass-sensitive sensors with the ability to detect minute changes (down to the ppb range) of masses caused by the incorporation of guest molecules into host layer.

The operating principle of QMBs is well documented,[38−40] outlined in Figure 4, and an application of the principle to polyphenylene dendrimers has previously been reported.[37] As quantified in Table 1 and presented graphically in Figure 5, the hydrogenation of **14** to yield **16** causes a considerable decrease in the frequency shift, i.e., a diminishment of the number of guest molecules taken up by the dendrimer layer on the QMB detector surface.

Table 1 lists the frequency shift $\Delta\nu$ and the number of guest molecules calculated thereof according to the formula:[41−43] $N_g = (\Delta\upsilon 4.4 \times 10^{-9} N_A)/M_A$ an $N_{cd} = (4.4 \times 10^4 N_A \times 10^{-9})/M_d$, where N_g = number of guest molecules, N_A = Avogadro's number (6.024×10^{23}), M_A = molecular mass of analyte (guest), M_d = molecular mass of dendrimer (host), and N_{cd} = number of coating dendrimer molecules.

In order to compare the pre- and post-hydrogenated dendrimers with regard to their capacity to incorporate guests, the number of host molecules in the coating must be known.

Whereas this number can be calculated for the hydrogenated forms, it is unavailable for the non-hydrogenated species because their diameter d is not known with certainty. However, the relations $d(\mathbf{16}) \leq d(\mathbf{14})$ and $d(\mathbf{15}) \leq d(\mathbf{12})$ hold to the effect that the number of coating dendrimer molecules should be equal or slightly larger for **15** and **16** than for **12** and **14**. This reinforces the conclusion that the 1,2-ethanediyl forms are less apt to include guests than the 1,2-ethynediyl forms.

The lower propensity of the hydrogenated dendrimer **16** to the binding of guest molecules is readily explained by the fact that in **16** the flexibility of the 1,2-ethanediyl links allows conformations in which neighboring phenylene units can engage in mutual $\pi-\pi$ interaction, leading to a more compact form of the dendrimer in which free space between the dendrons is reduced. Entering guest molecules, therefore, must compete with these intramolecular $\pi-\pi$ interactions and the free energy change accompanying host−guest interaction is less favorable than in the case of the rigid 1,2-ethynediyl containing dendrimer for which the voids already exist. Note that the QMB experiment involves reaction of the solid layer on the sensor surface with guest molecules from the gas phase; therefore, both dendrimers **14** and **16** exist in nonsolvated from. It may be argued that the transformation **14** → **16** constitutes a chemical change in which triple bonds are eliminated and this is the reason for the reduced ability of **16** to accept guest molecules. However, in view of the vast number of benzene rings present as sites for $\pi-\pi$ interaction with guest molecules, the elimination of eight −C≡C− triple bonds would not be sufficient to explain the ca. 30% reduction in guest molecule binding. Figure 5 also demonstrates that the attenuation of the hosting ability, brought about by hydrogenation, is chemically unspecific in that all substrates employed experience the same reduction factor of incorporation. This suggests that in all cases the loss of intramolecular voids is the chief reason which renders the inclusion of guest molecules less favorable for **16** than for **14**.

Conclusions

The inclusion of 1,2-alkynediyl units is an alternative to *p*-phenylene segments in the construction of rigid-arm exploded dendrimers. The 1,2-alkynediyl unit offers the possibility of hydrogenation and thereby the chance to compare size and hospitality of the dendrimers upon transition from the rigid to a more flexible form. Given the enormous steric shielding in the environment of the −C≡C− triple bonds, it came as a surprise that the heterogeneous hydrogenation actually took place under fairly normal conditions. Hydrogenation very probably causes a decrease in the diameter of the 1,2-alkynediyl-containing dendrimer with concomitant reduction of the internal porosity. In this situation, the incorporation of guest molecules must compete with intradendrimer $\pi-\pi$ interactions, and this aspect is primarily responsible for the decrease in guest molecule uptake exhibited by the hydrogenated dendrimers compared to their non-hydrogenated precursors.

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