Spherical polyphenylene dendrimers *via* Diels–Alder reactions: the first example of an A_4B building block in dendrimer chemistry

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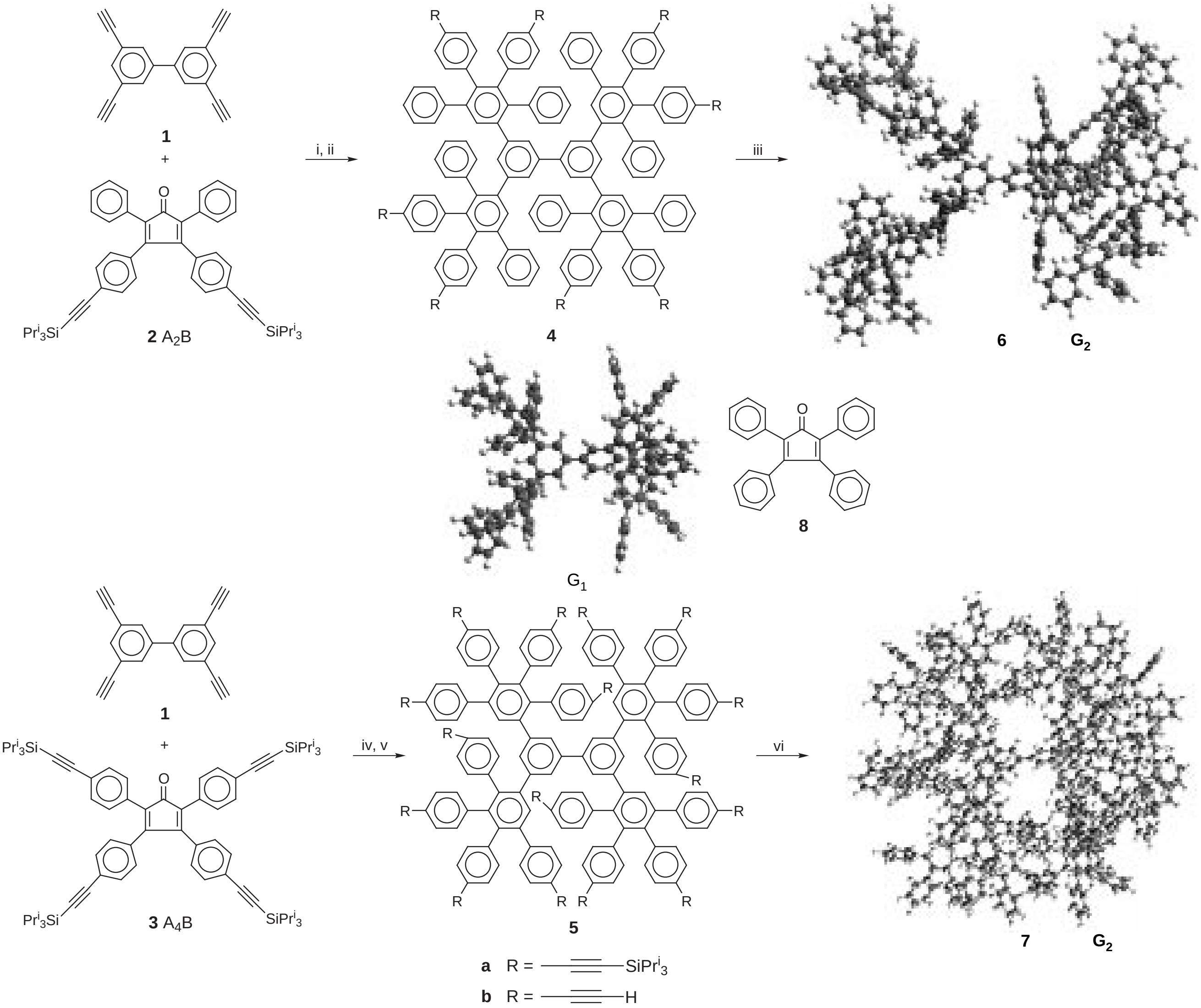
The [2+4]cycloaddition of the novel A_4B building block 2,3,4,5-tetrakis(4-triisopropylsilylethynylphenyl)cyclopenta-2,4-dienone 3 with 3,3’,5,5’-tetraethynylbiphenyl 1 allows the rapid synthesis of a spherical polyphenylene nanoparticle with 102 benzene rings.

Dendrimers form highly symmetric layered molecules that adopt a spherical shape at higher generations.[1,2] The three-dimensional form of dendrimers is determined by the core, the interior building blocks and the surface groups. Our synthetic approach towards polyphenylene dendrimers is based on the selective Diels–Alder cycloaddition of 3,4-bis(4-triisopropylsilylethynylphenyl)-2,5-diphenylcyclopenta-2,4-dienone **2** with the four dienophile functions of 3,3’,5,5’-tetraethynylbiphenyl **1**.[3,4] Compound **2** reacts only as diene since the triisopropylsilyl (TIPS) groups make the ethynyl functions inaccessible for dienophiles (see Scheme 1). The TIPS groups of the first dendrimer generation **4a** can be removed quantitatively using Bu_4NF and the resulting **4b** can undergo another [2+4]cycloaddition with **2**. This cycloaddition-deprotection sequence allows the synthesis of a third generation dendrimer, consisting of pentaphenylbenzene units, which has a diameter of about 5 nm according to computer generated ball-and-stick models.[4] As revealed by molecular dynamics simulations on the second



Scheme 1 *Reagents and conditions:* i, Ph_2O–α-methylnaphthalene (1 : 1), 180–200 °C, 14 h, 89%; ii, Bu_4NF, THF, 25 °C, 5 h, > 98%; iii, **8**, Ph_2O–α-methylnaphthalene (1 : 1), 180–200 °C, 15 h, 86%; iv, Ph_2O–α-methylnaphthalene (1 : 1), 180–200 °C, 14 h, 77%; v, Bu_4NF, THF, 25 °C, 5 h, 87%; vi, Ph_2O–Bu^tOMe (8 : 11), 190 °C, 44 h, 62%

generation dendrimer **6**, the higher dendrimer generations represent shape-persistent nanoparticles.

Here we investigate the influence of the branching unit on the shape of the dendrimer employing **1** as core and a four-directional A_4B building block **3** rather than the A_2B building block **2**. Thereby, we introduce 2,3,4,5-tetrakis[4-triisopropylsilylethynylphenyl)cyclopenta-2,4-dienone **3** as a powerful multifunctional reagent that allows the rapid construction of a spherical polyphenylene architecture.

Cyclopentadienone **3** contains four dienophile units and one diene function and can thus be regarded as an A_4B building block which represents, to the best of our knowledge, the first example of a dendrimer branching element possessing a multiplicity higher than 3.[5] Compound **3** was prepared by the base-catalyzed condensation of 4,4'-bis(triisopropylsilyl)benzil and 1,3-bis(4-triisopropylsilylethynyl)acetone (83%, red crystals).[6] The acetone was obtained *via* the Sonogashira coupling[7] of triisopropylsilylacetylene and 1,3-di(4-bromophenyl)acetone (82%). The latter was synthesized by converting 4-bromobenzyl bromide with $Fe(CO)_5$ in the presence of NaOH under phase transfer conditions (CH_2Cl_2–H_2O; 43%).

The four-fold Diels–Alder reaction of the A_4B building block **3** with the tetraethynylbiphenyl **1** led to the first dendrimer generation **5a** (77%, white solid). After cleaving the TIPS groups (**5b**), further reaction with **3** provided a mixture of products, determined by mass spectrometry, consisting of the desired sixteen-fold Diels–Alder product, and mainly of the fourteen-fold [2+4]cycloaddition product.† In contrast, addition of tetraphenylcyclopentadienone **8** to **5b** led smoothly to the desired sixteen-fold Diels–Alder product **7** exclusively, which was isolated as a white solid in 62% yield (see Scheme 1).

The different results obtained by the reaction of **5b** with **2** or **3** can be easily rationalized by looking at ball-and-stick models, which were generated using the MM2 (85) force field with the CERIUS 2 program package and applying the Conjugate Gradient 200 algorithm (compare Scheme 1):[8] As expected, the appearances of the corresponding first generations **4** and **5** are very similar, as both dendrimers contain 22 benzene rings and differ only in the number of substituents, while having the same spatial extension. The corresponding second generations already exhibit clearly dissimilar shapes. The dendrimer **6**, with 62 benzene rings, synthesized using the A_2B building block **2**, possesses a dumb-bell like structure, whereas the use of the A_4B building block **3** leads to 'nanoball' architecture **7**, which possesses 102 benzene rings. As the second generations of both dendrimers have a maximum extension of about 4 nm, the density of benzene rings is dramatically increased in **7**. In the case of the more strongly branched dendrimer **7** the space available for a new dendrimer shell is sufficient to accommodate the incoming eighty unsubstituted benzene rings spherically around the dendrimer core. The fact that the 64 sterically demanding TIPS groups of the A_4B building blocks cannot be accommodated, proves the concept of densest packing.[9,10] The preferred formation of the fourteen-fold cycloaddition product can be understood according to Tomalia as a sterically induced stoichiometry.[11]

The obtained dendrimers exhibit unexpectedly good solubility in common organic solvents such as toluene and CH_2Cl_2. Therefore, they can be fully characterized by matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) as well as ^1H and ^{13}C NMR spectroscopy. The perfect agreement between calculated and experimentally determined m/z ratios for the dendrimers as well as GPC analysis confirm their monodispersity.§ With respect to the physical properties of the dendrimers their thermal stability is noteworthy. The thermogravimetric analysis yielded decomposition temperatures well above 450 °C for the TIPS substituted and 580 °C for the unsubstituted dendrimers under air.

The special features of the results presented above can be summarized as follows: (i) in contrast to the established concept based on metallo-organic coupling reactions for the construction of polyphenylene dendrimers[12] (as well as the closely related hyperbranched polyphenylenes),[13] the growth of the dendrimers presented here is achieved *via* [2+4]cycloaddition followed by a desilylation; (ii) using the A_4B building block **3** and the core **1** the second dendrimer generation exhibits properties such as spherical shape in spite of the core's D_{2h} symmetry and the densest packing of benzene rings which one would generally expect only for higher generation numbers; (iii) using a defined dendrimer core, the shape of the dendrimer formed depends on the cyclopentadienone used.

Our current investigations involve light scattering experiments on higher dendrimer generations as well as microscopic visualization after adsorption on substrate surfaces.

Notes and References

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‡ The amount of higher Diels–Alder cycloaddition products can be increased by repeated treatment with cyclopentadienone **2b**.

§ *Selected data* for **3**: FD-MS: m/z 1105, calc. for $C_{73}H_{100}OSi_4$: 1106; δ_H (200 MHz, CD_2Cl_2, 303 K) 7.37–7.28 (m, 8H), 7.17 (d, ^3J 8.0, 4H, H_{Aryl}), 6.89 (d, ^3J 8.0, 4H, H_{Aryl}), 1.13 (s, 84H, H_{TIPS}); δ_C(75 MHz, CD_2Cl_2, 303 K) 199.7 (**C**=O), 154.8, 133.5, 132.5, 132.4, 131.4, 130.8, 130.1, 126.2, 124.8, 123.5, 107.7 [Ar*C*≡CSi(Pr^i)$_3$], 107.3 [Ar*C*≡CSi(Pr^i)$_3$], 93.4 [ArC≡*C*Si(Pr^i)$_3$], 92.7 [ArC≡*C*Si(Pr^i)$_3$], 19.2 [CH(*C*H$_3$)$_2$], 12.1 [*C*H(CH$_3$)$_2$]; mp 296 °C (decomp.). For **7**: MALDI-TOF-MS: m/z 7762, calc. for $C_{612}H_{410}$: 7764; δ_H(500 MHz, THF, 303 K) 7.70–7.34 (br, 24H), 7.25–6.03 (br, 386H); δ_C(125 MHz, THF, 303 K) 145.55, 145.45, 145.36, 144.60, 144.54, 144.43, 144.22, 144.18, 144.05, 144.03, 143.99, 143.91, 143.87, 143.80, 143.73, 143.69, 143.62, 143.58, 143.45, 142.99, 142.86, 142.80, 142.69, 142.64, 142.56, 135.60, 135.50, 135.45, 135.38, 135.33, 135.29, 135.16, 135.09, 135.02, 134.95, 134.87, 134.76, 134.70, 134.65, 134.57, 133.49, 133.38, 133.34, 130.92, 130.29, 130.24, 130.18, 129.95, 129.86, 129.55, 129.49, 129.04, 128.87, 128.72, 128.60, 109.67; GPC analysis (polystyrene as standard): $M_w/M_n = 1.04$; mp > 300 °C.

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