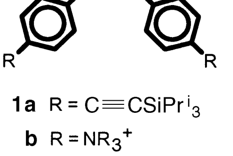
Nanosized polyphenylene dendrimers based upon pentaphenylbenzene units

Frank Morgenroth, Christian Kübel and Klaus Müllen*

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

A facile divergent synthesis of monodisperse polyphenylene dendrimers having diameters of 21–55 Å is presented. These nanoparticles have been prepared *via* a [2+4]cycloaddition–deprotection sequence using an excess of tetraphenylcyclopentadienone **1a** as monomer and the tetraethynylbiphenyl **2** as core. Due to the dense packing of 22, 62 or 142 benzene rings in generations G_1, G_2 and G_3, respectively, the conformational freedom of the higher generations G_2 and G_3 is limited. Molecular mechanics calculations as well as molecular dynamics simulations are included in a discussion of the structure and the shape-persistence of G_2. The calculations revealed that selected inner distances of the molecule varied only 5–10% during the molecular dynamics simulations, thus indicating that the overall shape of the molecule essentially did not change throughout the simulation time.

Within the past decade, chemists have established new methods to synthesize complex molecules and also to control their macromolecular and supramolecular architecture. These efforts are connected tightly to a transition in molecular scale from the picometre to the nanometre range.[1] Supramolecular chemistry and nanostructure engineering assemble organic and inorganic molecules using covalent as well as non-covalent interactions to obtain complex systems such as liquid crystals or nanotubes.[2] By focusing on all-hydrocarbon, covalent bond-based dendritic nanostructures,[3–6] Moore and his co-workers built nanosized phenylacetylene dendrimers.[3] Hart *et al.* have reported the construction of polyaromatic iptycenes.[4] A remarkable feature of these nanostructures is their essentially invariant shape (shape-persistence).[7] Shape-persistence is a requirement for the design of nanoparticles with tailor-made topographic features and well-defined functional group dispositions. In the case of Moore's phenylacetylene-based macromolecules, shape-persistence was accomplished using rigid phenylacetylene subunits. The cascades of Hart are highly rigid due to the connection of bicyclo[2.2.2]octane moieties with benzenes. In this paper, we present an alternative route to generation G_3, of a new type of nanosized all-hydrocarbon dendrimers. Our idea for obtaining shape-persistence was to create an extremely dense packing of benzene rings, thereby limiting the conformational freedom of the dendrimer. Considering these structural aspects, we present molecular mechanics calculations of G_2, which provide insight into the three dimensional structure of this molecule. Additionally, in this report we will discuss molecular dynamics simulations investigating the shape-persistence of G_2.



1a $R = C\equiv CSiPr^{i}_{3}$

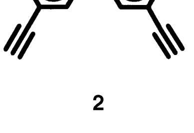
b $R = NR_3^+$

c $R = CN$

d $R = OH$

e $R = CO_2H$

f $R = (CH_2)_nCH_3$



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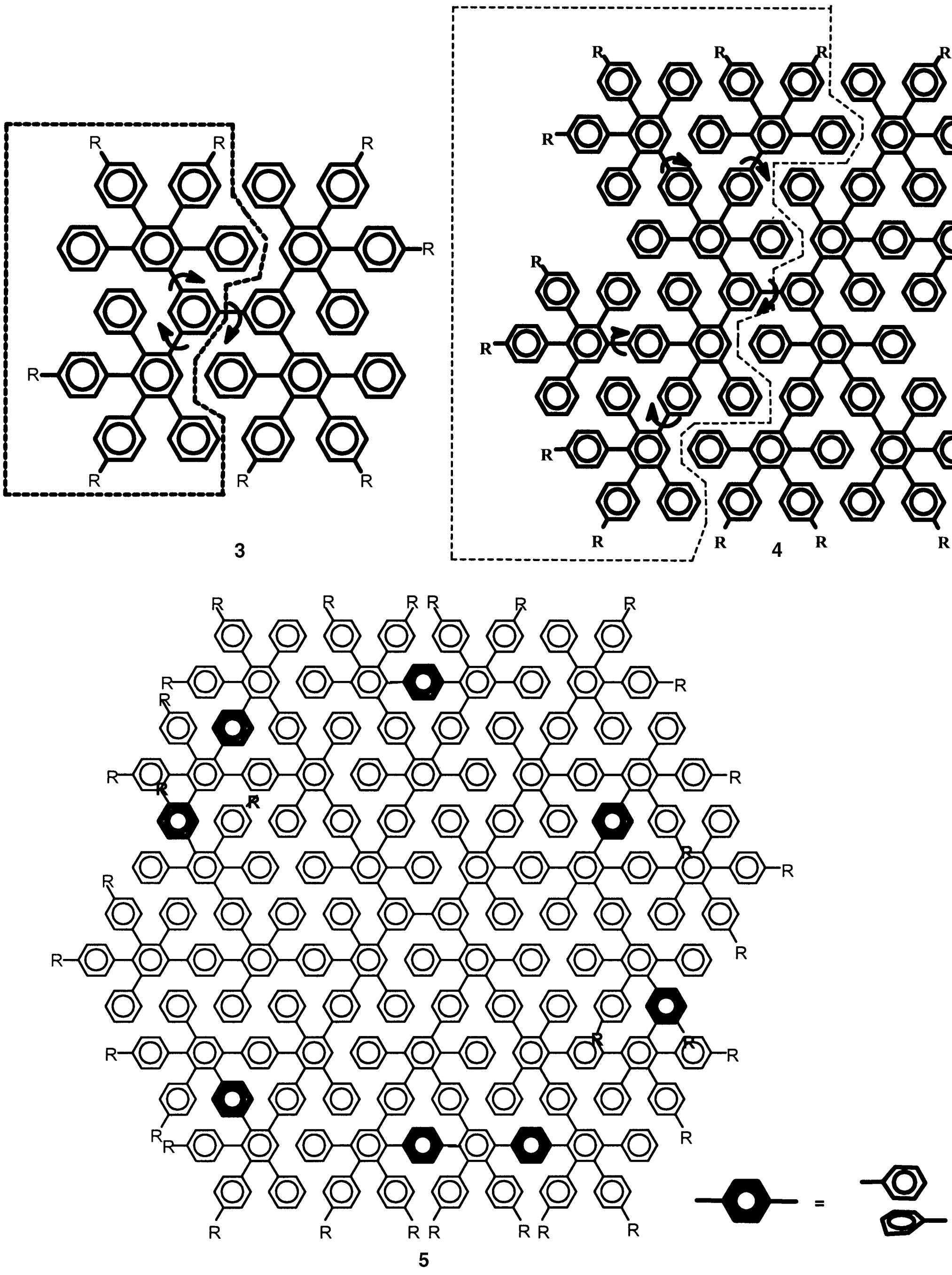
Results and Discussion

Synthesis

We have recently introduced 3,4-bis(4-triisopropylsilylethynylphenyl)-2,5-diphenylcyclopenta-2,4-dienone (**1a**) as a building block for the synthesis of monodisperse polyphenylene dendrimers such as **3a** and **4a** (Scheme 1).[8] A key step of our approach was the [2+4] cycloaddition of **1a** to a core such as 3,3′,5,5′-tetraethynylbiphenyl (**2**). Compound **1a** contained a diene function and two dienophile functions and could thus be considered an AB_2 building block. Since the two dienophile functions in **1a** were blocked by triisopropylsilyl groups, four equivalents of the tetraphenylcyclopentadienone **1a** could be reacted selectively in a four-fold [2+4] cycloaddition with the four dienophile functions of **2**. Under the applied reaction conditions (180 to 200 °C, diphenyl ether–a-methylnaphthalene 1 : 1) the Diels–Alder reaction proceeded with the loss of carbon monoxide to yield the first generation **3a** of the dendrimer. Compound **3a** was used for an eight-fold addition of **1a** after an easy deprotection with tetrabutylammonium fluoride (Bu_4NF) in THF resulting in the second generation **4a** (Scheme 1). As discussed below in detail, characterization was accomplished by mass spectrometry and ^1H and ^{13}C NMR spectroscopy.

This paper outlines the synthetic aspects of our dendrimer construction and its extension to the fabrication of G_3. The procedure employed worked for generation growth as well as activation both in high yields and with no significant side reactions. The yields of white amorphous polyphenylene dendrimers, from the Diels–Alder growth reaction, were higher than 80% and the deprotection reaction was nearly quantitative. However, the growth steps had to be optimized to avoid an incomplete reaction of the terminal ethynyl groups since this severely affected the growth scheme.

Simply heating a solution of 5 equiv. of **1a** and **2** in diphenyl ether–a-methylnaphthalene to 200 °C for 1 h led to a mixture of two-, three- and the desired four-fold Diels–Alder reaction product. As expected, this mixture could not be separated chromatographically. In contrast, a quantitative formation of G_1 was obtained by adding **2** in a-methylnaphthalene slowly to a hot solution of 5 equiv. of **1a** in diphenyl ether–a-methylnaphthalene. By focusing on the growth step from G_1 to G_2, a longer reaction time was essential to avoid growth imperfections. This was expected since our divergent approach required the cycloaddition to be carried out at an increasing number of ethynyl groups. In addition, the use of pentaphenyl substituted benzene rings as repetitive units resulted in a very



$$2 \xrightarrow{i} 3a \xrightarrow{ii} 3b \xrightarrow{i} 4a \xrightarrow{ii} 4b \xrightarrow{i} 5a$$

G_1 G_2 G_3

a R = $C{\equiv}CSiPr^i_3$
b R = $C{\equiv}CH$

Scheme 1 Chemical structure and procedure for the preparation of the polyphenylene dendrimer generations G_1 to G_3. The dotted lines mark 'half-G_1' and 'half-G_2', respectively (see text). Overlapping phenyl rings in the 2D projection of **5** are plotted in bold. *Reagents and conditions*: i, **1a**, heat; ii, Bu_4NF.

compact structure. Furthermore, steric crowding in the vicinity of the ethynyl groups had presumably lowered the reaction rate (see Fig. 1). Accordingly, the addition of **3b** to 5 equiv. **1a** at 180 to 200 °C over 2 h and an additional reaction time of the same time, yielded a mixture of seven- and eight-fold [2+4] cycloaddition product. However, the addition of **3b** over 5 h and an additional reaction time of 4 h selectively led to the desired eight-fold Diels–Alder product.

By extending this concept, the synthesis of G_3 was achieved by adding a mixture of **4b** and **1a** in diphenyl ether–a-methylnaphthalene to a solution of **1a** in diphenyl ether–a-methylnaphthalene at 180 to 200 °C over a period of 25 h. The mixture was stirred for an additional 15 h at 180 °C. In the case of G_3, the addition of fresh **1a** was required in order to sustain a sufficient excess of the cyclopentadienone during reaction, otherwise traces of 10- to 15-fold cycloaddition products were observed. The latter could be converted into **5a** by a second treatment with an excess of **1a**. We obtained **5a** as a white amorphous powder in 81% yield. A comparison of our divergent approach with the convergent synthesis of an

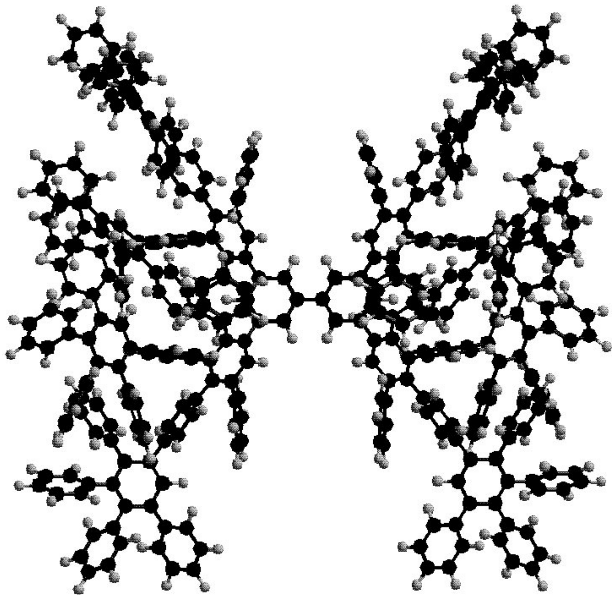


Fig. 1 The 3D structure of G_2 (without acetylene units) according to molecular mechanics calculations[12]

oligophenylene-dendrimer with 46 benzene rings carried out by Miller and Neenan[9] revealed that in our experiments a faster dendrimer growth, in terms of the number of benzene rings, was achieved in fewer steps and without the use of catalysts. Our synthetic approach has also enabled products to be purified simply by precipitation from acetone with ethanol.

The larger dendrimer generations G_2 and G_3, accessible by our process, had 62 and 142 benzene rings, respectively. We used computer models to estimate the dimensions of these nanoparticles. As an indication of the impressive size of our dendrimers, the diameters of G_2 and G_3 were found to be approximately 38 and 55 Å (Table 1).

The success of our dendrimer synthesis was complemented by the full characterization of the new structures.

Characterization

Mass spectrometry is an excellent tool for determining the purity and structural composition of dendrimers.[10] The triisopropylsilyl-protected as well as the oligoethynyl substituted dendrimers exhibited an unexpectedly good solubility in common solvents such as dichloromethane, acetone or tetrahydrofuran (THF). Therefore, characterization was performed using matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) as well as ^1H and ^{13}C NMR spectroscopy. By ^1H NMR spectroscopy it was only possible to check the correct intensity ratio of aromatic and aliphatic (or acetylenic) protons.[11] Employing MALDI-TOF-MS allowed potential growth imperfections during the [2+4] cycloaddition to be detected without any ambiguity, even at the higher generations, since each unreacted ethynyl group caused a mass difference of *ca.* 717 g mol^{-1} (**1a** less CO) relative to the completely reacted product. The perfect agreement between calculated and experimentally determined *m*/*z* ratios for G_1 to G_3 confirmed the monodispersity of the dendrimers (see Experimental).

Table 1 Summary of the molecular mass and the approximate diameter of the dendrimers. These diameters were estimated from molecular models generated using the CERIUS^2 program

generation	formula	formula mass/ g mol^{-1}	number of benzene rings	diameter/Å
G_0, **2**	$C_{20}H_{10}$	250	2	7
G_1, **3b**	$C_{148}H_{90}$	1868	22	21
G_2, **4b**	$C_{404}H_{250}$	5104	62	38
G_3, **5b**	$C_{916}H_{570}$	11577	142	55

Computer simulations

Molecular mechanics calculations[12] performed for G_1 and G_2 (without acetylene units) provided a first insight into the 3D structure of the dendrimers (Fig. 1). In the first step, one half of the molecule (see Scheme 1) was optimised by energy minimisation using 144 and 1024 different conformers (obtained by torsion about the marked bonds in Scheme 1) of G_1 and G_2, respectively. Thereby we obtained one conformer for 'half-G_1' (see Scheme 1) with an energy 3 kcal mol^{-1} (1 cal = 4.184 J) lower than any other and another 20 conformers differing by less than 10 kcal mol^{-1}. This observation was even more pronounced in the case of 'half-G_2' (see Scheme 1 and Fig. 1), where we found more than 100 conformers differing by less than 15 kcal mol^{-1}. In both cases we used the conformer with the lowest energy to generate the complete dendrimer. This was finally optimised by varying the torsional angle of the central phenyl–phenyl unit (bond a, see Fig. 2). The latter was generated by connecting two 'half-G_2' to obtain G_2 itself.

Therefore, we obtained a 3D structure of G_2, which could be regarded as consisting of a twisted central biphenyl unit carrying four branches which were nearly orthogonal to the central biphenyl unit. The two pentaphenylbenzene units in each branch were twisted. They were nearly parallel to each other, but the protons of the central phenyl rings pointed in different directions (Fig. 1). The dimensions of the dendrimer G_2, in the three main directions, were 36, 27 and 14 Å according to the molecular mechanics calculations.

The existence of several local energy minima of similar energy is a requirement for a flexible molecule, but the dynamic behaviour is controlled by the activation energy for transforming the conformers into one another. A first insight into the dynamic behaviour of the dendrimer was gained by molecular dynamics (MD) simulations[13] of G_2. We analysed the trajectory of the MD simulations by inspecting specific intramolecular distances and torsional angles (specified in Fig. 2 and summarized in Table 2) to obtain information about the motions within the dendrimer.

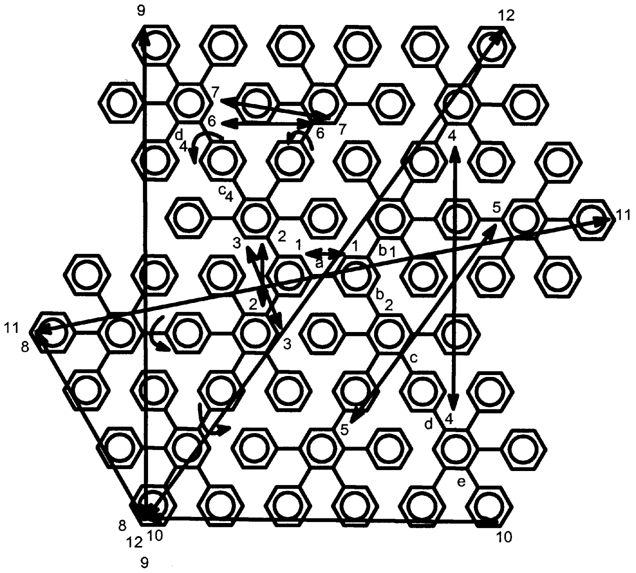


Fig. 2 2D projection of G_2 (without acetylene units). The distances and torsional angles used to determine intramolecular rotations and the overall shape of the dendrimer G_2 are labelled.

Table 2 Intramolecular distances and torsional angles (values obtained by MD simulations,[13] compare Fig. 2) used to determine intramolecular rotations and the overall shape of the dendrimer G_2

number	distance/Å (%)	torsion	angle/°
1	2.8 ± 0.16 (± 5.3)	a	20–60
2	4.7 ± 0.15 (± 3.2)	b_1	115–140
3	6.7 ± 0.25 (± 3.7)	b_2	-25–(-50)
4	17.1 ± 1.3 (± 7.3)		
5	11.3 ± 1.0 (± 8.8)		
6	7.4 ± 0.6 (± 8.0)		
7	8.0 ± 1.0 (± 12.5)		
8	13.8 ± 1.0 (± 7.2)		
9	27.5 ± 2.5 (± 9.1)		
10	31.0 ± 1.5 (± 4.8)		
11	34.2 ± 1.7 (± 5.0)		
12	35.8 ± 2.2 (± 6.1)		

The observed distribution of distances had several reasons. There were three (approximately) independent motions: vibration, rotation and bending of the oligophenylenes. In order to distinguish between these motions we compared two distance distributions: a distance sensitive to the rotations of interest and one with similar connectivity, but being insensitive to any rotation (for example, distances 2 and 3 or 6 and 7, Fig. 2). The difference between both distributions was assumed to be due to independent rotations. Furthermore, the corresponding torsional angles revealed that the rotations were (nearly) frozen or that they were correlated strongly.

The calculations indicated the following qualitative picture for the internal rotations of the dendrimer:

- We observed a rotation of the central phenyl–phenyl unit (bond a) with the torsional angle varying by ±20° and an average torsional angle of *ca.* 40°. The average torsional angle was not the one found during the energy minimization, instead a continuous change of the torsional angle of bond a was observed throughout the equilibration time (distance 1, torsional angle of bond a).
- A rotation about bond b was observed (torsional angle of bond b_1 and b_2), but this rotation was accompanied only by a small change in distance 3, thus indicating a strongly correlated rotation of both branches of the dendrimer. The same results were obtained by comparing distances 4 and 5.
- There was an (partially) independent rotation of the pentaphenylbenzene units about the bonds c_4 or d_4 (comparison of the distances 6 and 7).

In spite of the aforementioned rotations, the overall shape of the molecule changed only slightly. The distances 8 to 12 generated a network measuring the diameter of the dendrimer in several directions. All these distances changed by only ±5 to 10% throughout the whole simulation time, thereby indicating that the dendrimer was a shape-persistent molecule. We suppose that this behaviour was due to the high packing density of phenylene rings, which caused the strongly correlated rotations within the molecule. Thus the shape-persistent dendrimer retained some flexibility which enhanced solubility in common solvents. In addition, the phenylene groups carrying the functional groups (acetylene units) in G_2 were pointing out of the dendrimer during the whole simulation time. Therefore, the functional groups were exposed for further reaction and had a well-defined chemical environment due to the shape-persistence of the dendrimer.

The next generation, G_3, had an even higher packing density of phenylene units. We expected the different branches of this dendrimer to be even more correlated (details have yet to be revealed by further MD simulations) resulting in an even more shape-persistent 3D structure with a diameter of *ca.* 55 Å.

Summary and Outlook

Our innovative approach can be summarized as follows:

- A simple synthetic process led quickly to nanosized molecules with well-defined size and shape.
- A new type of polyphenylene dendrimer based on pentaphenylbenzene units was obtained.
- The synthesized materials were soluble in common organic solvents and, therefore, were readily processable.
- It was possible to control the chemical functionalization of the nanoparticles.

With respect to the last point, it should be mentioned that we are working on the functionalization of our dendrimers. A straightforward approach would be a final Diels–Alder reaction with tetraphenylcyclopentadienones carrying functional groups such as $-NR_3^+$ (**1b**), $-CN$ (**1c**), $-OH$ (**1d**), $-COOH$ (**1e**) or $-(CH_2)_nCH_3$ (**1f**). Such groups are relevant for chemical, physical and potentially catalytic properties.[14] Our approach uses charged as well as neutral lipophilic or hydrophilic and hydrogen-bonding substituents. In addition, units which facilitate the covalent coupling of electronically active components such as redox-systems (in particular viologen), dyes, NLO-phores or active metal complexes are attractive. The synthesis of such species is the subject of our current investigations.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 500 MHz on a Bruker DRX 500 spectrometer. ^{13}C NMR spectra were recorded on the same instrument at 125 MHz. Chemical shifts are given in parts per million (ppm) using the solvent signal as reference;[15] *J* values are in Hz. Mass spectral analyses were carried out on ZAB2-SE-FPD (VG Analytical) and Bruker Reflex-TOF. MALDI-TOF-MS spectra were measured using 1,8,9-trihydroxyanthracene as matrix. Compounds **1a** and **2** were prepared from commercially available starting materials by methods to those already in literature.[16–18]

Generation G_1, 3a, 3b

To a degassed solution of **1a** (3.27 g, 0.00440 mol) in a mixture of diphenyl ether–a-methylnaphthalene (3 ml/3 ml), **2** (55.0 mg, 0.220 mmol) in a-methylnaphthalene (2 ml) was added over 30 min at 180–200 °C under a stream of argon. After stirring for 30 min at this temperature the mixture was allowed to cool. The cold reaction mixture was diluted with methanol (40 ml) and stirred overnight at 25 °C. A crude red product was filtered. Contaminating **1a** was removed either by reprecipitating from acetone with ethanol or by passage of the crude product through a short column of silica gel using light petroleum–dichloromethane (3:1) as eluent. Yield: 0.611 g (0.196 mmol, 89%) white amorphous solid, mp 169–170 °C. MS *m/z* (FD): 3118 (M^+, 100%), calc. for $C_{220}H_{250}Si_8$ 3119. Deprotection was achieved by adding tetrabutylammonium fluoride (0.820 g, 3.14 mmol) to a stirred solution of **3a** (0.611 g, 0.196 mmol) in THF (50 ml). After stirring for 5 h at 25 °C, the THF was evaporated under reduced pressure to give a yellow solid, which was taken up in acetone. The resulting solution was added dropwise to ethanol (100 ml). The desired product precipitated as white solid and was filtered. Deprotection was nearly quantitative, mp > 300 °C, d_H (500 MHz, CD_2Cl_2, 303 K): 7.25–7.21 (br, 12 H), 7.14–6.97 (br, 28 H), 6.88–6.68 (br, 38 H), 6.45–6.38 (br, 4 H), 3.03–3.00 (br, 8 H). d_C (125 MHz, CD_2Cl_2, 303 K): 141.54, 141.49, 141.27, 141.11, 141.00, 140.67, 140.04, 139.31, 138.66, 132.11, 131.87, 131.84, 131.79, 131.18, 130.88, 130.31, 128.12, 127.64, 127.01, 126.93, 126.50, 119.80, 119.50, 83.78, 77.43, 77.33. MS *m/z* (MALDI-TOF): 1907 in the presence of K, calc. for $C_{148}H_{90}K^+$, 1907.

Generation G_2, 4a, 4b

Preparation of **4a** and **4b** was analogous to **3a** and **3b** except for the reaction time of the [4+2] cycloaddition. Compound **3b** was added over 5 h to the hot reaction mixture and the solution was allowed to stir for an additional 4 h. Yield: 87%, white amorphous solid, **4a**, mp > 300 °C. MS *m/z* (MALDI-TOF): 7645 in the presence of K, calc. for $C_{548}H_{570}Si_{16}K^+$, 7645.

4b, mp > 300 °C, d_H (500 MHz, CD_2Cl_2, 303 K): 7.46–6.45 (br, 388 H), 3.03–2.99 (br, 404 H). d_C (125 MHz, CD_2Cl_2, 303 K): 142.22, 141.71, 141.66, 141.29, 141.22, 141.12, 140.41, 139.90, 139.48, 139.39, 138.95, 138.56, 131.90, 131.84, 131.43, 131.30, 131.15, 130.86, 130.46, 130.22, 128.92, 128.60, 128.08, 127.98, 127.37, 126.89, 126.27, 126.19, 121.31, 119.77, 119.46, 102.69, 83.80, 77.39, 77.33.

Generation G_3, 5a

Compound **1a** (1,87 g, 2.51 mmol) was taken up in a mixture of diphenyl ether–a-methylnaphthalene (8 ml/8 ml). The stirred solution was degassed and heated to 180–200 °C under argon. Then a degassed solution of **4b** (80.0 mg, 0.0157 mmol) and **1a** (1.17 g, 1.57 mmol) in a mixture of diphenyl ether–a-methylnaphthalene (5 ml/5 ml) was added dropwise over 25 h under a stream of argon. After the addition was complete, the reaction mixture was allowed to stir for an additional 15 h at 180 °C. The cold reaction mixture was diluted with methanol (40 ml) and stirred overnight at 25 °C. The crude red product was filtered and reprecipitated from acetone with ethanol. Yield: 210.9 mg (0.0127 mmol, 81%), white amorphous solid, mp > 300 °C, d_H (500 MHz, CD_2Cl_2, 303 K): 7.43–6.41 (br, 538 H), 1.21–0.99 (br, 672 H). d_C (125 MHz, CD_2Cl_2, 303 K): 142.21, 141.89, 141.50, 141.24, 141.12, 140.77, 140.40, 140.33, 140.04, 139.54, 139.46, 138.92, 138.65, 138.51, 138.21, 131.81, 131.40, 131.20, 131.05, 130.78, 130.45, 130.22, 128.90, 128.59, 128.10, 127.96, 127.40, 127.23, 126.85, 126.24, 121.18, 120.88, 119.22, 107.30, 90.95, 90.86, 18.80, 18.45, 11.93, 11.71, 11.48. MS *m/z* (MALDI-TOF): 16619 in the presence of K, calc. for $C_{1204}H_{1210}Si_{32}K^+$, 16619.

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11 Due to the limited accuracy of the integration, traces of side products due to incomplete [2+4] cycloaddition could not be detected by ^1H NMR spectroscopy, but appeared in the MALDI-TOF-MS as distinguished peaks.

12 The molecular mechanics calculations were carried out using the MM2 (85) forcefield with the CERIUS^2 program package and applying the Conjugate Gradient 200 algorithm. G_1 and G_2 were minimized by considering only one half of the molecule. In the case of G_1, two torsional angles b_1 and b_2 (as shown in Fig. 2) were varied stepwise by 30°, whereas four torsional angles were varied in the case of G_2 (as shown in Fig. 2) in 45° steps. In a second step, two of those 'half-molecules' were connected and the torsional angle of this newly created, central phenyl–phenyl bond was optimised.

13 NVT-molecular dynamics simulations were carried out at 300 K (temperature dumping, 0.1 ps relaxation time) with a time step of 0.001 ps. For the evaluation of the molecular shape a simulation time of 35 ps was used after an initial equilibration time of 5 ps. Intramolecular distances were calculated by averaging the distances measured for every tenth conformer, torsional angles were measured every ps.

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