Solvophobically-driven 3-D self-assembly of "exploded"-type polyphenylene dendrimers†‡

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Received (in Montpellier, France) 4th December 2006, Accepted 7th March 2007
First published as an Advance Article on the web 26th March 2007
DOI: 10.1039/b617667b

Downloaded by University of Belgrade on 01 January 2013
Published on 26 March 2007 on http://pubs.rsc.org | doi:10.1039/B617667B

The three-dimensional self-assembly of a shape-persistent third-generation polyphenylene dendrimer into an extensively interdigitated hexamer was studied with ultra-high-mass MALDI-TOF mass spectrometry and dynamic light scattering. Remarkably, the high-precision assembly occurs in the absence of electrostatic or hydrogen-bonding interactions, and is the product of Lilliputian solvophobic interactions, mediated by the dendrimer arm size and shape. The assembly size can be tuned from monomer to dimer to hexamer simply by varying the solvent composition. Further growth or chain end densification results in fundamentally different aggregation or in disruption of the perfect packaging of the macromolecules. This hexameric structural motif is completely different than what has been previously accessible with conventional self-assembly and marks the beginning of a new direction in 3D nanofabrication.

Introduction

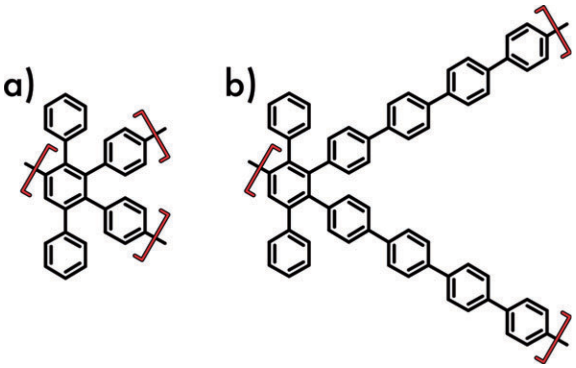
A strategy for the development of 3-D nanofabrication[1] hinges on the availability of suitable building blocks with defined shape and a mechanism for assembling and connecting them. To this aim, constructions from DNA[2], including polyhedra[3–5] and 2-D algorithmic assembly,[6] and from coordination chemistry[7–10] have thus far been most promising candidates.

Dendrimers have been proposed for use as tectons in the construction of nanoscale objects.[11] Most dendrimers are conformationally flexible, which limits their use in well-defined 3-D assembly. For structural control over large length scales, building blocks with reduced conformational freedom are required; otherwise, the shape of the molecule will be conformationally averaged and thus, lost. Polyphenylene dendrimers,[12] constructed from iterative Diels–Alder syntheses, are structurally perfect, shape-persistent,[13] and thermally stable molecules. They are made up of propeller-like pentaphenylbenzene repeat units, and connected by oligo(*p*-phenylene) spacers of different lengths (Scheme 1). Linear extension of the spacer directly translates into a larger molecule,[14] given the mostly radial branching directions and rigid backbone. The primary consequence is that large intramolecular cavities are present which can be solvent-filled in solution. In this context, the solubility of the backbone plays a major role in determining the physical properties of the molecules.

The "exploded" [**G3e**] polyphenylene dendrimer (Scheme 2), with 32 triisopropylsilylethynyl (T*i*PS) chain ends on the surface, whose composition is chemically distinct from that of the phenylene backbone, is potentially amphiphilic. Described herein is the 3D self-assembly of third-generation "exploded"-type polyphenylene dendrimers.

Results and discussion

Aggregation is an intrinsic property for rigid, conjugated π-systems such as 1-D oligo(phenylene ethynylene)s[15] and oligo(*p*-phenylene)s[16,17] in solution. Few examples have been reported of the reversible discrete aggregation of dendrimers[18,19] (not including dimers from phenylene-containing[20–22] or other dendrimers[23]), which are inherently three dimensional. Leveraging the monodisperse aspect of dendrimers, matrix-assisted laser desorption (MALDI) time of flight (TOF) mass spectrometry (MS) has been used to identify aggregation processes.[19,20,24] The MALDI-TOF mass spectra of "exploded"-type polyphenylene dendrimers were measured



Scheme 1 Polyphenylene dendrimer branching units: standard (a) and "exploded" (b).

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† This paper was published as part of the special issue on Dendrimers and Dendritic Polymers: Design, Properties and Applications.

‡ Electronic supplementary information (ESI) available: Calculation of theoretical dimensions, Fig. S1: MALDI mass spectrum for [**G3e**]-capped "dimer". See DOI: 10.1039/b617667b

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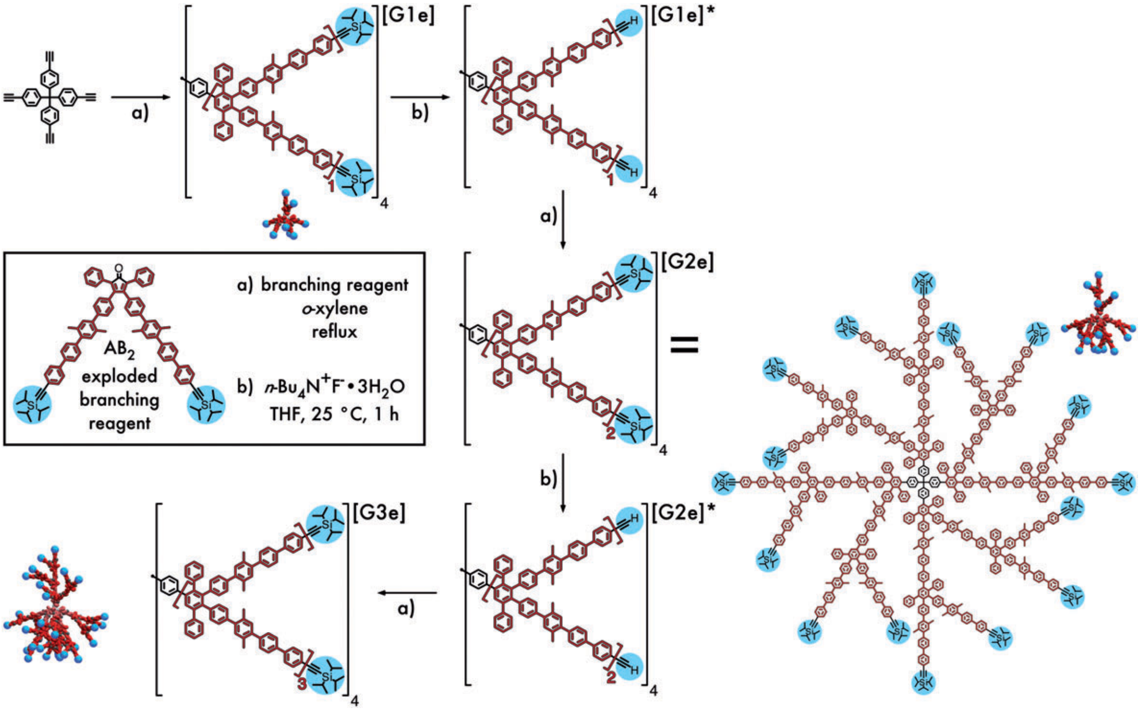

Scheme 2 Iterative synthesis of a third-generation, [**G3e**], polyphenylene dendrimer with oligo(*p*-phenylene) spacers and triisopropylsilylethynyl (TiPS) chain ends. Diels–Alder cycloadditions and cleavage of TiPS protecting groups are quantitative at each stage. Depicted are the simplified chemical structures and the 3-D, fully extended, roughly spherical geometries, resulting from the "mostly radial" branching geometry. The full repeat unit is highlighted by the one open and two closed red brackets.

using cryodetection for sensitive, high mass ion detection.[25] Cryodetection decreases the detector refresh time, which prevents saturation effects and is critical to measure accurately distributions of ions at high mass range. In addition to the molecular ion, the mass spectrum for the [**G2e**] dendrimer revealed a broad distribution of aggregates (Fig. 1(a)). The open nature of these dendrimers is exemplified by the extent of aggregation in all directions resulting from interdigitation of multi-dendrimer phenylenes. The third-generation dendrimer, which has a substantially higher surface density, was not expected to show the same behavior. Indeed, in addition to the molecular ion (31.1 kDa), the MALDI-TOF mass spectrum of the [**G3e**] polyphenylene dendrimer also yielded a distribution of aggregates but with a maximum population for the hexamer (Fig. 1(b)). Laser heating of these dendrimers has been observed[14] due to an overlap of the absorption spectrum with the laser wavelength used to ionize the dendrimer, and increasing the laser power above a critical level is known to fragment polyphenylene dendrimers. As such, a minimum amount of power is employed to obtain the MALDI signals. A further decrease is the laser power is not practical, but identification of specific noncovalent interactions using MALDI is enhanced by acquiring data only for the first laser shot on a fresh portion of the sample, minimizing laser heating of the same spot.[26,27] Using this "first shot mode," the hexamer of [**G3e**] was observed (186.6 kDa) almost exclusively (Fig. 1(c)), suggesting that the hexamer predominated during the solution-phase preparation but is disrupted upon heating during volatilization.

The nature of the solvophobic interactions, which drives the aggregation of dendrimers into clusters, is mediated by the sample preparation. Evaporation of the solvent from a solution of the dendrimer containing the matrix compound necessitates that the solution take on more the character of the matrix compound than the solvent. Dithranol, the matrix used, is more polar than THF, and an increase in the concentration of a polar component is known to induce aggregation in aromatic systems.[28] However, the hexamer also predominated in a preparation from a less polar matrix, DCTB,[29] instead of dithranol. This suggests that at high concentration, the dendrimer–dendrimer interactions outweigh the specific solvation of the dendrimer by the matrix, or in other words, that the dendrimer is remarkably self-complementary. The MALDI sample preparation induces aggregation, but the geometric properties of the dendrimer with respect to the orientations and sizes of the aggregating backbone results in assembly rather than non-specific aggregation.

The hexameric assembly resulted on the timescale of the MALDI sample preparation and is evidence for the limited degrees of freedom of the molecule. Given that each linear oligo(phenylene) segment formed from the repeat units and spacers is appreciably shorter than any value of polyphenylene persistence length,[30–33] the conformational flexibility is almost entirely from bond rotations and is limited. Combining solvophobic interactions with the possibility for extensive interdigitation and the knowledge of the strong preference for the hexamer permits only one valid structural motif: an octahedron (Fig. 2(c)). Likely, the first step in the assembly process is the partial segregation of the backbone from solution by interdigitation (Fig. 2(b)) of two 15-nm shape-persistent dendrimers (Fig. 2(a)). The degree of interdigitation by each

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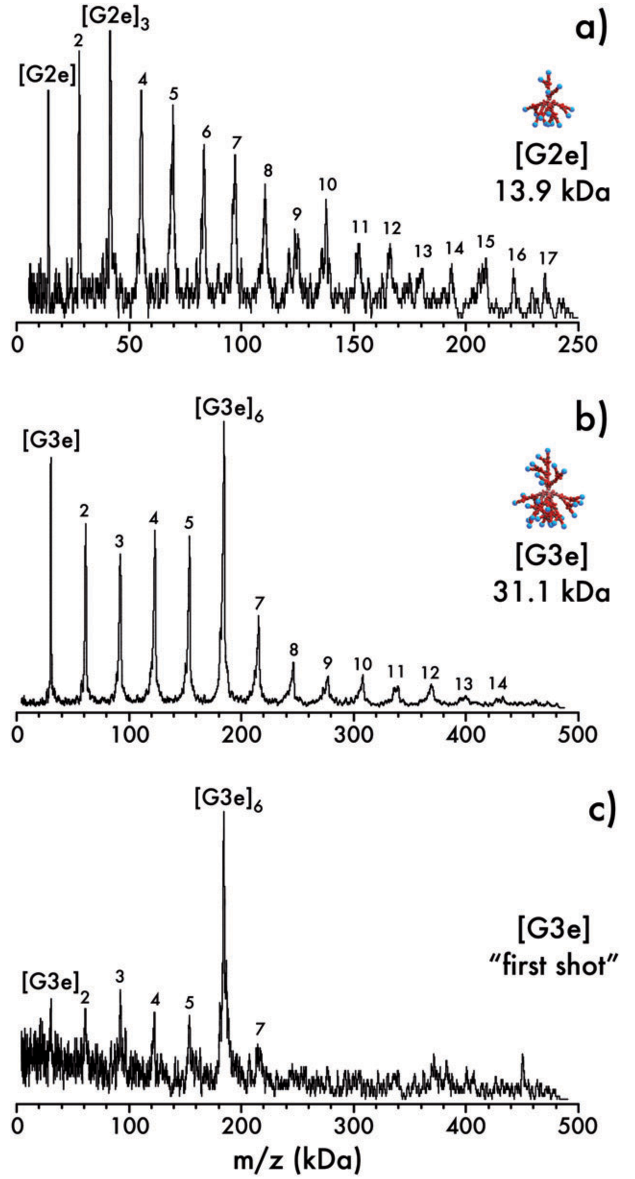

Fig. 1 MALDI-TOF mass spectra of dendrimers [**G2e**] (a), [**G3e**] (b) and [**G3e**] with single laser pulse irradiation of the sample spots or "first shot" (c). All were prepared by deposition from THF with dithranol as matrix.

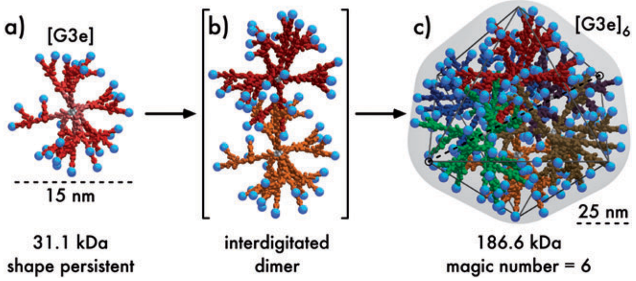

Fig. 2 Proposed model for the preferential assembly of [**G3e**] dendrimers (a) into a hexamer. The first stage of assembly is an interdigitated dimeric intermediate (b) where the π-surface of the oligophenylene is better shielded from solvent. Four additional dendrimers then interdigitate equatorially into the preformed dimer to form a pseudo-octahedral assembly, (c) maximizing contact between all dendrons. The extent of interdigitation was estimated using the hydrodynamic radius of an assembly in THF–hexane.

dendrimer in the pseudo-octahedral dendrimer complex, is not known, but the resulting assembly must accordingly be more dense than the parent dendrimer. The gas-phase observation after ionization of such large clusters formed by self-complementary self-assembly in solution is evidence that a large number of noncovalent interactions hold the individual dendrimers together. This has only been previously observed for biological macromolecules.[34] Stabilization of such an object would transform it into an ideal building block for 3D nanofabrication.[1]

Evaluation of the solution-phase assembly of the dendrimer under equilibrium conditions, rather than the kinetically trapped MALDI sample preparation conditions, was made with dynamic light scattering (Fig. 3). The hydrodynamic radius in THF, a good solvent, is 5.0 nm. Addition of an equal volume of hexane ($\chi_{\mathrm{THF}} = 0.61$[19,35]), a bad solvent for the phenylene backbone, but a good solvent for the T*i*PS chain ends, which are surface bound due to the shape persistent nature of the backbone, resulted in an increase of the hydrodynamic radius to 6.1 nm. An additional consequence of the dendrimer's shape persistence is that the hydrodynamic radius is not strongly influenced by the solvent. The increase in hydrodynamic size must then be attributed to aggregation. Given that the dendrimer hydrodynamic radii for both measurements are significantly smaller than the theoretical radius of the longest oligo(*p*-phenylene) arm, 7.6 nm, the prolate spheroid model[36] cannot be used to explicitly determine the extent of interdigitation, but the results are consistent with the formation of a dimer upon the addition of hexane (Fig. 4). Addition of more hexane ($\chi_{\mathrm{THF}} = 0.39$) results in a shift of the hydrodynamic radius to 12.6 nm, requiring a higher density of T*i*PS groups to solubilize the cluster, which is in strong agreement with the formation of the hexamer with assembly according to the above-described model (Fig. 2). Addition of more THF (to above $\chi_{\mathrm{THF}} = 0.75$) immediately disassembles the clusters. The presence of both good and bad solvent components permits reorganization of the dimer during further aggregation, which is not kinetically trapped, into a cluster whose size is consistent with the hexamer. Comparison to conical phase segregating monodendrons,[37,38] which also exhibit small aggregation number phenomena, can be drawn here, but the distinct difference is that this larger poly(phenylene) dendrimer amphiphile is globular and is far below bulk density, even in the aggregates.

Described elsewhere[19] is the assembly of higher-generation dendrimers, [**G4e**]–[**G6e**], which form predominantly tetramers in the mass spectrum. This switch in aggregation motif is believed to result in part from the densification of chain ends, whereby six molecules do not pack efficiently together. In addition, the highest generation dendrimers have a greater propensity for bending as they approach and exceed the persistence length of polyphenylene.[30–33] In an effort to understand more about the mechanism for self-assembly of [**G3e**], each ethyne of the [**G3e**] dendrimer was unmasked and capped (Scheme 3) with the standard AB_2 Diels–Alder poly(phenylene) building block, 3,4-bis-

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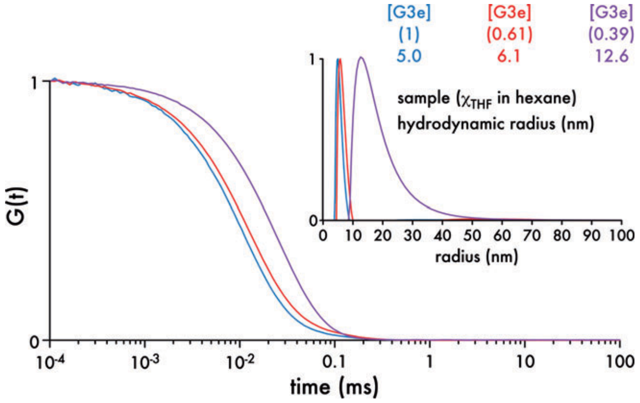


Fig. 3 Dynamic light scattering (DLS) results of [**G3e**] in THF and THF–hexane mixtures at 35 °C. CONTIN fits of hydrodynamic radius distributions, shown at right, are linearly mass weighted.

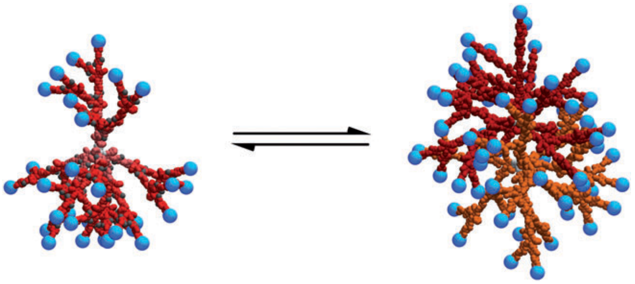
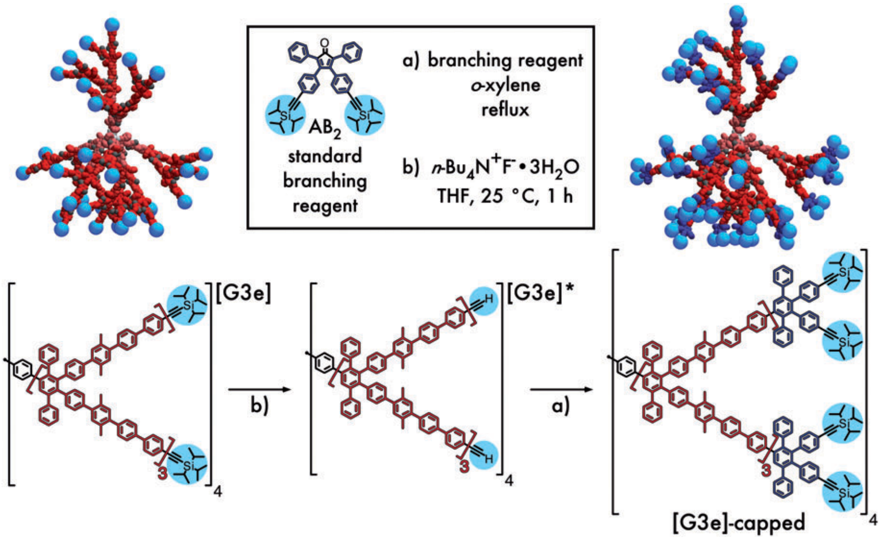


Fig. 4 Solvophobic dimerization of [**G3e**].

(4-(triisopropylsilylethynyl)phenyl)-2,5-diphenylcyclopentadienone.[39] The size exclusion chromatograph (SEC) of [**G3e**]-**capped** (Fig. 5(a)) contains a high molecular weight shoulder, which is incidentally not present for any dendrimer generation until [**G5e**]. These shoulders are not the result of a chemical side reaction, which has been shown not to occur over 128 reactions per molecule,[19] but are instead interlocked dimers resulting from aggregation during synthesis. The shoulder was separated by SEC (Fig. 5(b)) for further analysis. Complete synthetic details are given in the Experimental section.

The perfect aggregation of [**G3e**]-**capped** was expected to be hindered by the bulkier chain ends while maintaining shape persistence and would either result in extended aggregation, as in the case of [**G2e**], or in smaller aggregation numbers, as in the case of [**G4e**]. The "first shot" MALDI mass spectrum (Fig. 6) of [**G3e**]-**capped** revealed mostly dimer (98.1 kDa) and trimer (147.1 kDa), not the hexamer as observed for [**G3e**]. The molecular ion (49.0 kDa) was observed only when "first shot" was not used. The spectrum was qualitatively similar to the sample with the high molecular weight fraction removed. The amount of "dimer" formed in the synthesis was quite small, and the amount available for analysis after fractionation also very small. As such, the MALDI mass spectrum was only recorded at low concentration. The mass spectrum, although it has very low signal (ESI‡) compared with noise, monomer through tetramer are all observed, confirming that the dimer is physical, not chemical. Furthermore, all of the ions in the mass spectrum are singly charged, removing any doubt of the molecular perfection. Chain end functionalization (or "capping") [**G3e**] with the standard instead of the "exploded" building block provides the same number of chain ends as [**G4e**] but is denser in the periphery. The [**G3e**]-**capped** dendrimers do not fit well enough together to form a hexamer or even significant quantities of tetramer, at least on the timescale of the MALDI sample preparation.

The solution-state aggregation of the [**G3e**]-**capped** dendrimer was further investigated with dynamic light scattering as a function of the solvent composition (Fig. 7). The hydrodynamic radius in THF is 5.6 nm (theoretical radius 8.4 nm) with an increase to 7.7 nm upon addition of hexane (χ_{THF} = 0.61). The [**G3e**]-**capped** "dimer" was found to have a similar hydrodynamic radius of 8.0 nm in pure THF, which is further evidence of the interlocking of a small amount of interdigitated dendrimers during synthesis (Fig. 8). Increasing the



Scheme 3 Synthesis of [**G3e**] dendrimers "capped" with poly(phenylene) dendrons, [**G3e**]-**capped**.

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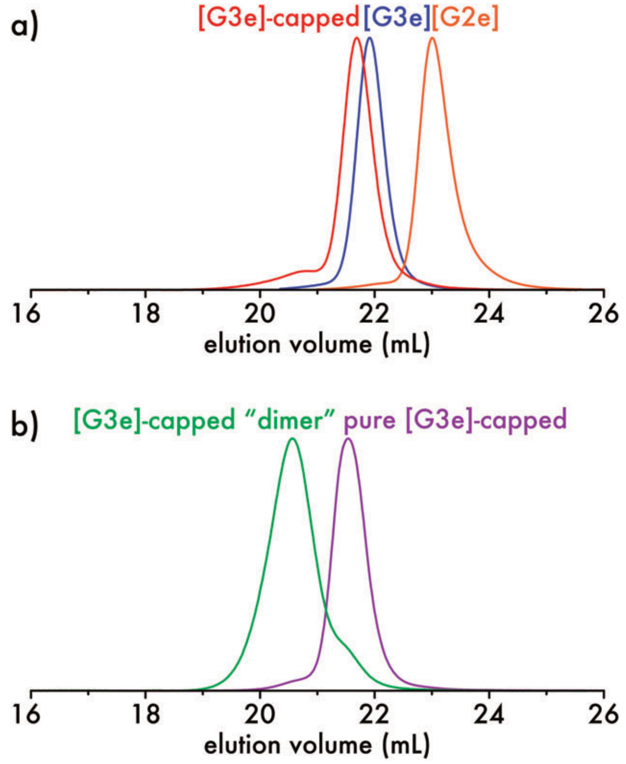

Fig. 5 Size exclusion chromatography (SEC) results of [**G2e**], [**G3e**], [**G3e**]-**capped** dendrimers (a), and fractionated [**G3e**]-**capped** dendrimer and its "dimer."

hexane content (χ_{THF} = 0.39) of the [**G3e**]-**capped** sample gives rise to much larger particles, but with the distribution maximum at 9.8 nm, significantly smaller than that of the [**G3e**] hexamer. This is furthermore consistent with the mass spectrometry results that the packing is not perfect and gives smaller aggregates with exposed solvophobic patches, some of which aggregate non-specifically to much larger species. The uncapped [**G3e**] dendrimer is a special case, where the highly symmetric surface areas of dendrimers are perfectly complementary for magic number self-recognition without generating extended structures.[18,21,22,40]

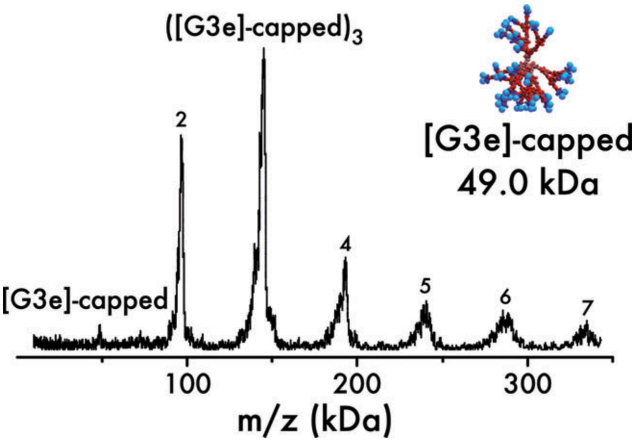

Fig. 6 "First shot" MALDI-TOF mass spectrum of the [**G3e**]-**capped** dendrimer, prepared by deposition from THF with dithranol as matrix.

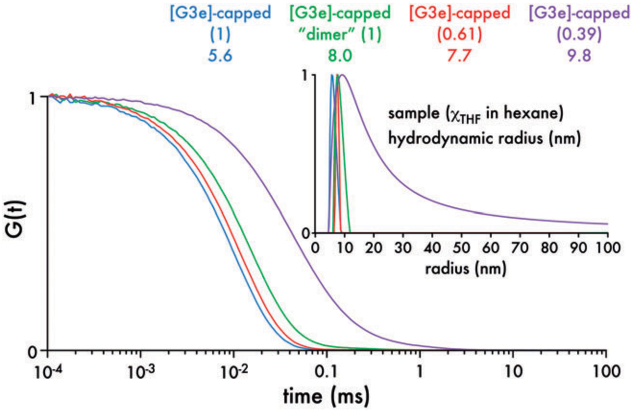

Fig. 7 Dynamic light scattering (DLS) results of the fractionated [**G3e**]-**capped** dendrimer and its "dimer" in THF and the [**G3e**]-**capped** dendrimer in THF–hexane mixtures at 35 °C. CONTIN fits of hydrodynamic radius distributions, shown at right, are linearly mass weighted.

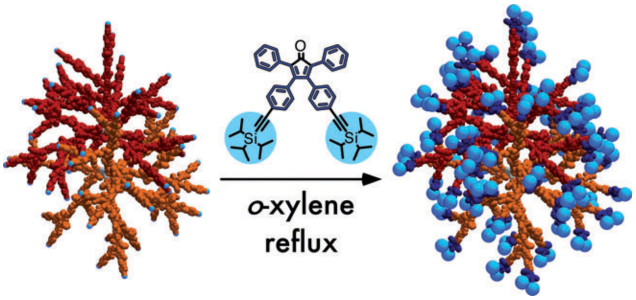

Fig. 8 Model of interlocked dimer formation during "capping" of [**G3e**]*.

Conclusions

The consequence of symmetric, stiff, radially oriented dendrons and chain ends with an open but globular structure is an unprecedented rapid and reversible 3D self-assembly of macromolecules for [**G3e**] using only interactions between oligophenylenes, which are inside the shell of surface-bound, but soluble chain ends. The assembly size is tuned from monomers with approximately tetrahedral symmetry, to dimer, and to a pseudo-octahedral hexamer simply by tuning the solvent polarity. A systematic construction along different length scales leads to a build up in complexity[41] such that structural hierarchies can be made with high precision. Increased generational growth or shell densification fundamentally change the assembly behavior, and the largest assemblies do not result. The assembly results without requiring the chain ends to be the aggregating component, which leaves them available for hierarchical constructions or for a possible function. In addition, a large number of interior functionalities remain which could be leveraged for covalent stabilization and the next phase of 3D nanofabrication as well for as host–guest chemistry.

Experimental

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX500 and AMX700 NMR spectrometers using the residual proton

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or the carbon signal of the deuterated solvent as an internal standard. ^{1}H NMR spectra were acquired at elevated temperature in deuterated tetrachloroethane to increase the mobility of the phenyl rings and reduce line widths.

Size exclusion chromatography (SEC) was performed in THF at room temperature using a 515 pump (Waters), 717 plus injector (Waters), 10 μm guard column, and SDV GPC columns with 500 Å, 10^4 Å and 10^6 Å porosities (PSS, Mainz), UV S-3702 (SOMA) (at 254 nm) and RI ERC 7512 refractive index (ERMA Inc.) detectors. SEC data analysis was performed using PSS-WinGPC (PSS, Mainz). The nature of the porosity of the dendrimers as hosts for small quantities of solvent impurities as well as incomplete combustion limit the effectiveness of elemental analyses for polyphenylene dendrimer samples.[14]

Elemental analyses of dendrimers with these generations were not performed. As such, MALDI-TOF in combination with ^{1}H NMR was relied upon more heavily.

Computations were performed with a dual 2 GHz G5 processor PowerMac (Apple Computer, Cupertino) equipped with 2 GB RAM. Semi-empirical AM1 calculations on oligo (phenylene)s were performed with Spartan '04 for Macintosh (Wavefunction, Inc., Irvine). Three-dimensional models were constructed in custom-written POV-Ray (www.povray.org) scripts that used the geometric properties obtained from the AM1 calculations.

Materials

Dendrimers $C(Ph([G2e](ethynyl\text{-}T\textit{i}PS)_4)_4$ (**[G2e]**), $C(Ph[G3e](ethynyl\text{-}T\textit{i}PS)_8)_4$ (**[G3e]**) and $C(Ph([G3e](ethyne)_8)_4$ (**[G3e]***) based on the building block 3,4-bis{2′,5′-dimethyl-4‴-triisopropylsilylethynyl-1,1′:4′,1″:4″,1‴-quaterphenyl-4-yl}-2,5-diphenylcyclopentadienone[14] were synthesized according to the literature. The **[G3e]-capped** dendrimer was synthesized analogously using 3,4-bis(4-(triisopropylsilylethynyl)-phenyl)-2,5-diphenylcyclopentadienone,[39] the standard AB_2 building block for the Diels–Alder syntheses of polyphenylene dendrimers. Dithranol (1,8,9-anthracenetriol) was used as received from Fluka. THF was freshly distilled before use. DCTB was used as received from Fluka. All other chemicals were used as received from Fluka or Aldrich.

Mass spectrometry

Mass spectrometry data was collected using a macromizer MALDI-TOF prototype instrument (Comet; Flamatt, Switzerland). This instrument was designed specifically for the detection of high mass ions by cryodetection. The instrument incorporates special ion focusing optics to direct ions onto the superconducting tunnel junction cryodetector.[25] This cryodetector provides mass independent ion detection as well as a very fast refresh time, which prevents detector saturation effects. Mass independent detection is obtained because the cryodetector measures the entire kinetic energy of the impacting particle (ions) and does not rely merely on a high ion velocity for ion detection. Detector saturation becomes a problem in time-of-flight experiments when lower mass ions, which arrive first at the detector, effectively turn off channels of the detector, thereby decreasing sensitivity for the later arriving high mass ions. These two factors make cryodetection ideal for the detection of very high masses, particularly from polymer samples which may contain high mass signals (above a MDa) and signals over a large mass range (20 kDa–2 MDa).

For the mass spectrometric analysis of **[G2e]** and **[G3e]**, the MALDI preparation was made by preparation of a solution of dithranol in THF (0.25 M). The dendrimer sample (*ca.* 0.1 mg) was added to the solution (10 μL). The solution (1 μL) was then spotted on the polished stainless steel MALDI plate directly. Standard macromizer conditions were used consisting of a 20 kV source voltage, which is lowered by 3 kV for extraction after a delay time of 4 μs. Data were collected for 200 laser shots. Peak identifications for all ions were made initially using a low molecular weight calibrant. An external master calibration curve ($R^2 = 0.9999$) was constructed using the flight times and the theoretical average masses for the second- through sixth-generation dendrimers (not shown) and their respective clusters. The presented data have had the final master calibration applied. Because the MALDI data was acquired with a cryodetector which measures the kinetic energy of the impacting ions, it was possible to discern multiply charged ion signal from singly charged ion signal.[42] The ions shown are all singly charged.

It should also be noted that Comet has discontinued production of the macromizer. Currently there is no commercial cryodetector mass spectrometer available; however, alternative high mass detectors (CovalX, Zürich) may prove effective.[43]

Dynamic light scattering technique-photon correlation spectroscopy (DLS)

Intensity correlation functions $g^{(2)}(q,t)$ were recorded by an ALV-5000E digital full correlator (ALV, Langen, Germany) at a scattering angle $\theta = 90°$ using an Nd-YAG laser (Verdi, Coherent) operating at $\lambda = 532$ nm and 10 mW single mode intensity on the sample. The detection was made using two avalanche photodetectors in pseudo-cross-correlation mode to remove unwanted contributions from correlated after-pulses inherent in this type of detector. Data analysis was performed using the CONTIN[44,45] inverse Laplace fitting routine. The resulting distribution of radii was normalized by mass. The $g^{(2)}(q,t)$ curves were normalized to a contrast of one.

Sample solutions for DLS were prepared in pure THF at 1 mg mL^{-1}, were filtered through 0.2 μm porosity PTFE filters, and were allowed to equilibrate for 1 day prior to diluting to the final solution concentration. Dilution was always made to the dendrimer solution using the good solvent (THF) first, then slow addition of the requisite amount of bad solvent (hexane or methanol) to prevent precipitation. The solutions were equilibrated at 35 °C for more than 1 h prior to the DLS measurements at the same temperature. Literature values for the refractive index and viscosity were used for the THF–hexane mixtures.[46]

Synthesis

$C(Ph[G3e][G'1](ethynyl\text{-}TiPS)_{16})_4$ ([G3e]-capped). $C(Ph([G3e](ethyne)_8)_4$ (**[G3e]***) (50 mg, 0.002 mmol) was dissolved in *o*-xylene (3 mL) by heating to 100 °C and simultaneously

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degassed by bubbling with argon for 30 min. Under argon 3,4-bis(4-(triisopropylsilylethynyl)phenyl)-2,5-diphenylcyclopentadienone (142 mg, 0.191 mmol) was added, and the reaction mixture was heated in a sealed tube at reflux for 5 d. After cooling to room temperature, the reaction mixture was precipitated into hexane and filtered. The precipitate was washed with copious amount of hexane, acetone, and methanol to obtain a colorless powder (91 mg, 98%). ^{1}H NMR (500 MHz, 350 K, $C_2D_2Cl_4$): δ 7.62–6.70 (m, 1716 H, Ar), 2.22, 2.20, 2.08, 2.06, 2.04, 2.02 (m, 336 H, CH_3) and 1.05 (br, 1344 H, T*i*PS) ppm; ^{13}C NMR (175 MHz, 350 K, $C_2D_2Cl_4$): δ 142.40, 142.37, 142.27, 142.20, 142.15, 142.12, 142.05, 141.78, 141.23, 141.16, 141.07, 140.99, 140.93, 140.87, 140.82, 140.44, 140.40, 140.40, 140.33, 140.30, 140.27, 139.93, 139.62, 138.93, 138.77, 138.55, 132.89, 132.57, 132.54, 131.90, 131.79, 131.75, 131.60, 131.56, 131.01, 130.80, 130.74, 130.65, 130.39, 130.18, 129.88, 127.97, 127.80, 127.37, 126.64, 126.19, 126.09, 121.11, 120.85, 107.91, 107.84, 90.51, 90.33, 20.13, 20.00, 19.97, 19.80, 18.92 and 11.76 ppm; MALDI TOF (dithranol): exact mass calc. for $[M]^+$ $C_{3649}H_{3396}Si_{64}$: 49048, found: 49164 $[M]^+$.

Acknowledgements

The research is supported by the Deutsche Forschungsgemeinschaft (DFG) in the frame of the Sonderforschungsbereich (SFB) 625 and the Swiss National Science Foundation (Grant 200020-103616). This support is gratefully acknowledged by the authors. C. G. C. is grateful for financial support from a U.S. National Science Foundation MPS Distinguished International Postdoctoral Research Fellowship (MPS-DRF) (Award: DMR-0207086) and from the Max Planck Society.

References

1 R. C. Merkle, *Nanotechnology*, 2000, **11**, 89–99.
2 N. C. Seeman, *Nature*, 2003, **421**, 427–431.
3 Y. Zhang and N. C. Seeman, *J. Am. Chem. Soc.*, 1994, **116**, 1661–1669.
4 W. M. Shih, J. D. Quispe and G. F. Joyce, *Nature*, 2004, **427**, 618–621.
5 R. P. Goodman, I. A. T. Schaap, C. F. Tardin, C. M. Erben, R. M. Berry, C. F. Schmidt and A. J. Turberfield, *Science*, 2005, **310**, 1661–1665.
6 P. W. K. Rothemund, *Nature*, 2006, **440**, 297–302.
7 S. Leininger, J. Fan, M. Schmitz and P. J. Stang, *Proc. Natl. Acad. Sci. USA*, 2000, **97**, 1380–1384.
8 B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield and P. J. Stang, *J. Am. Chem. Soc.*, 1999, **121**, 10434–10435.
9 N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794–796.
10 (*a*) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 3644–3662; (*b*) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J.-M. Lehn, *Angew. Chem.*, 2004, **116**, 3728–3747.
11 D. A. Tomalia, *Prog. Polym. Sci.*, 2005, **30**, 294–324.
12 U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser and K. Müllen, *Macromolecules*, 2001, **34**, 187–199.
13 (*a*) S. Rosenfeldt, Nico Dingenouts, D. Pötschke, M. Ballauff, A. J. Berresheim, K. Müllen and P. Lindner, *Angew. Chem., Int. Ed.*, 2004, **43**, 109–112; (*b*) S. Rosenfeldt, Nico Dingenouts, D. Pötschke, M. Ballauff, A. J. Berresheim, K. Müllen and P. Lindner, *Angew. Chem.*, 2004, **116**, 111–114.
14 (*a*) E. V. Andreitchenko, C. G. Clark, Jr., R. E. Bauer, G. Lieser and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 6348–6354; (*b*) E. V. Andreitchenko, C. G. Clark, Jr., R. E. Bauer, G. Lieser and K. Müllen, *Angew. Chem.*, 2005, **117**, 6506–6512.
15 D. J. Hill, M. J. Mio, R. B. Prince, T. Hughes and J. S. Moore, *Chem. Rev.*, 2001, **101**, 3893–4011.
16 W.-Y. Yang, E. Lee and M. Lee, *J. Am. Chem. Soc.*, 2006, **128**, 3484–3485.
17 Y.-S. Yoo, J.-H. Choi, J.-H. Song, N.-K. Oh, W.-C. Zin, S. Park, T. Chang and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 6294–6300.
18 D. Liu, S. De Feyter, M. Cotlet, U.-M. Wiesler, T. Weil, A. Herrmann, K. Müllen and F. C. De Schryver, *Macromolecules*, 2003, **36**, 8489–8498.
19 C. G. Clark, Jr., R. J. Wenzel, E. V. Andreitchenko, W. Steffen, R. Zenobi and K. Müllen, *J. Am. Chem. Soc.*, 2007, **129**, 3292–3301.
20 K. L. Walker, M. S. Kahr, C. L. Wilkins, Z. Xu and J. S. Moore, *J. Am. Soc. Mass Spectrom.*, 1994, **5**, 731–739.
21 S. Loi, U.-M. Wiesler, H.-J. Butt and K. Müllen, *Chem. Commun.*, 2000, 1169–1170.
22 S. Loi, U.-M. Wiesler, H.-J. Butt and K. Müllen, *Macromolecules*, 2001, **34**, 3661–3671.
23 J.-C. Blais, C.-O. Turrin, A.-M. Caminade and J.-P. Majoral, *Anal. Chem.*, 2000, **72**, 5097–5105.
24 (*a*) M. A. C. Broeren, J. L. J. van Dongen, M. Pittelkow, J. B. Christensen, M. H. P. van Genderen and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2004, **43**, 3557–3562; (*b*) M. A. C. Broeren, J. L. J. van Dongen, M. Pittelkow, J. B. Christensen, M. H. P. van Genderen and E. W. Meijer, *Angew. Chem.*, 2004, **116**, 3641–3646.
25 R. J. Wenzel, U. Matter, L. Schultheis and R. Zenobi, *Anal. Chem.*, 2005, **77**, 4329–4337.
26 L. R. H. Cohen, K. Strupat and F. Hillenkamp, *J. Am. Soc. Mass Spectrom.*, 1997, **8**, 1046–1052.
27 A. Wortmann, T. Pimenova, S. Alves and R. Zenobi, *Analyst*, 2007, **132**, 199–207.
28 M. Kastler, W. Pisula, D. Wasserfallen, T. Pakula and K. Müllen, *J. Am. Chem. Soc.*, 2005, **127**, 4286–4296.
29 L. Ulmer, J. Mattay, G. Torres-Garcia and H. Luftmann, *Eur. J. Mass Spectrom.*, 2000, **6**, 49–52.
30 B. L. Farmer, B. R. Chapman, D. S. Dudis and W. W. Adams, *Polymer*, 1993, **34**, 1588–1601.
31 U. B. Steiner, M. Rehahn, W. R. Caseri and U. W. Suter, *Macromolecules*, 1994, **27**, 1983–1984.
32 S. Vanhee, R. Rulkens, U. Lehmann, C. Rosenauer, M. Schulze, W. Köhler and G. Wegner, *Macromolecules*, 1996, **29**, 5136–5142.
33 G. Petekidis, D. Vlassopoulos, G. Fytas and G. Fleischer, *Macromolecules*, 1998, **31**, 1406–1417.
34 A. J. R. Heck and R. H. H. van den Heuvel, *Mass Spectrom. Rev.*, 2004, **23**, 368–389.
35 A concentration known to induce aggregation in polyphenylene dendrimers.
36 H. Brenner, *Int. J. Multiphase Flow*, 1974, **1**, 195–341.
37 X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey and J. K. Hobbs, *Nature*, 2004, **428**, 157–160.
38 (*a*) V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *Angew. Chem., Int. Ed.*, 2000, **39**, 1597–1602; (*b*) V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *Angew. Chem.*, 2000, **112** 1661–1666.
39 (*a*) F. Morgenroth, E. Reuther and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 631–634; (*b*) F. Morgenroth, E. Reuther and K. Müllen, *Angew. Chem.*, 1997, **109**, 647–649.
40 D. J. Liu, S. De Feyter, P. C. M. Grim, T. Vosch, D. Grebel-Koehler, U.-M. Wiesler, A. J. Berresheim, K. Müllen and F. C. De Schryver, *Langmuir*, 2002, **18**, 8223–8230.
41 G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418–2421.
42 G. C. Hilton, J. M. Martinis, D. A. Wollman, K. D. Irwin, L. L. Dulcie, D. Gerber, P. M. Gillevet and D. Twerenbold, *Nature*, 1998, **391**, 672–675.
43 R. J. Wenzel, S. Kern and R. Zenobi, in *American Society for Mass Spectrometry Annual Conference*, Seattle, WA, 2006.
44 S. W. Provencher, *Comput. Phys. Commun.*, 1982, **27**, 229–242.
45 S. W. Provencher, *Comput. Phys. Commun.*, 1982, **27**, 213–227.
46 S. L. Oswal, R. L. Gardas and R. P. Phalak, *J. Mol. Liq.*, 2005, **116**, 109–118.

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