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Synthesis and computer modelling of hydroxy-derivatised carbosilane dendrimers based on polyhedral silsesquioxane cores

Xinjie Zhang, Katherine J. Haxton, Loïc Ropartz, David J. Cole-Hamilton and Russell E. Morris *

School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, UK KY16 9ST. E-mail: rem1@st-and.ac.uk

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Divergent synthesis methods have been used to prepare 2nd generation dendrimers based on polyhedral silsesquioxane cores with up to 72 terminal groups at their surface. Repetitive hydrosilation/allylation of vinyl-functionalised polyhedral silsesquioxanes produce chlorosilyl- and allyl-derivatised dendrimers respectively. Hydroboration/oxidation of the allyl-functionalised dendrimers produces alcohol (hydroxy) terminated dendrimers. Energy minimisation and molecular dynamics techniques have been used to model the architectures of the dendrimers. The results show the dendrimers are relatively spherical, globular molecules, with a large proportion of the terminal hydroxy groups located in a shell at the exterior of the dendrimer. As the number of terminal groups on the dendrimers increases the number of the dendrimer branches that back fold towards the core of the dendrimer also increases.

Introduction

Dendrimers are highly branched regular monodisperse macromolecules. They are currently under investigation as biomimetic catalysts, building blocks for fabrication of designed materials, molecular carriers for chemical catalysts, and potential vehicles for delivery of drugs and immunogens,[1] and as selective molecular gates,[2] as well as light-emitting diodes, signal amplifiers, frequency converters and other photonic devices.[3]

Dendrimers are generally prepared using two approaches;[4] a divergent method where successive dendrimer layers (generations) are added to a core and a convergent method where the branches of the dendrimer are synthesized first and subsequently attached together at a focal point to produce the final molecule. A major drawback with dendrimer synthesis, especially the divergent method, is that it often requires many repetitive steps in order to build the dendrimer outwards leading to multi-step and often low yield preparations. This problem can be partially overcome by the use of polyhedral oligomeric silsesquioxanes (POSS) molecules as the core of the dendrimers. Octavinyl-POSS species (**1**) have eight terminal vinyl groups on the exterior of an almost cubic core.[5] Reaction at all eight of these terminal groups, with for example $HSiCl_3$, produces a 1st generation dendrimer with a relatively large number (24) of chloro-groups at the exterior of the molecule (POSS-24Cl, **2**). Vinylation of the dendrimer followed by further hydrosilation with $HSiCl_3$ will produce a dendrimer with 72 chloro groups (POSS-72Cl, **10**). In this way a dendrimer with a high number of terminal groups can be prepared in only three high-yielding synthetic steps. This reduces the number of steps required to produce such a high number of terminal groups compared to that needed for a core with, for example 4 terminal vinyl groups (*e.g.* tetravinylsilane). Importantly, this also reduces the need for wasteful isolation and purification steps during the synthesis. Another potential advantage of POSS-based dendrimers is the effect of the high multiplicity of the core on the structure of the molecule. The cubic shape and high multiplicity of the POSS core will, in principle, be amplified by the dendrimer branches to produce a fairly spheroidal, globular molecule with a large proportion of the terminal groups at or near the surface of the dendrimer, even at low generations. Our overall goal in preparing these highly functionalised dendrimers is to use them as supports for homogeneous catalysts, where the catalytic functionality is tethered to the exterior surface of the dendrimer to obtain the highest number of active sites possible.

Chloro-silyl or -vinyl dendrimers of the chosen generation number prepared using divergent methods can susbsequently be used as synthetic platforms for other, more useful functionality. We have prepared a number of POSS-based dendrimer molecules with functionality ranging from terminal silane (Si–H), silanol (Si–OH), aromatic aldehyde, carboxylic acid and Schiff base groups.[6,7] In addition, we have also prepared a number of phosphine functionalised dendrimers for use as catalytic ligands. Use of these molecules in combination with rhodium as the catalytic metal produce some very interesting and exciting results on the selectivity of hydroformylation reactions. Phosphines prepared from vinyl terminated dendrimers (*i.e.* with two carbons between the last silicon and the phosphorus atoms) show greatly improved selectivity (compared with similar small molecule catalysts) towards the preferred long chain aldehyde products.[8] On the other hand, those made from the Cl-functionalised dendrimers (with only one carbon between the Si and P atoms) show only a very small improvement over their small molecule analogues.[9] The length of the alkylene chain between the outermost silicon atom and the terminal functionality on the dendrimer is then very important.

In this paper we report the synthesis and characterisation of dendrimers with exterior allyl functionality that will form the basis of dendrimers with longer propylene spacer chains. In addition, the use of allyl functionality allows us to prepare hydroxy (alcohol) terminated dendrimers that are difficult to prepare from vinyl silanes because of competing elimination reactions. The hydroxyl-terminated dendrimers are very attractive materials because of their possible application as carriers of drugs and sensors,[10] as well as possible supports for homogeneous catalysts. We also report molecular modelling studies aimed at determining their likely shapes and the distribution of the end groups around the surface of the dendrimers.

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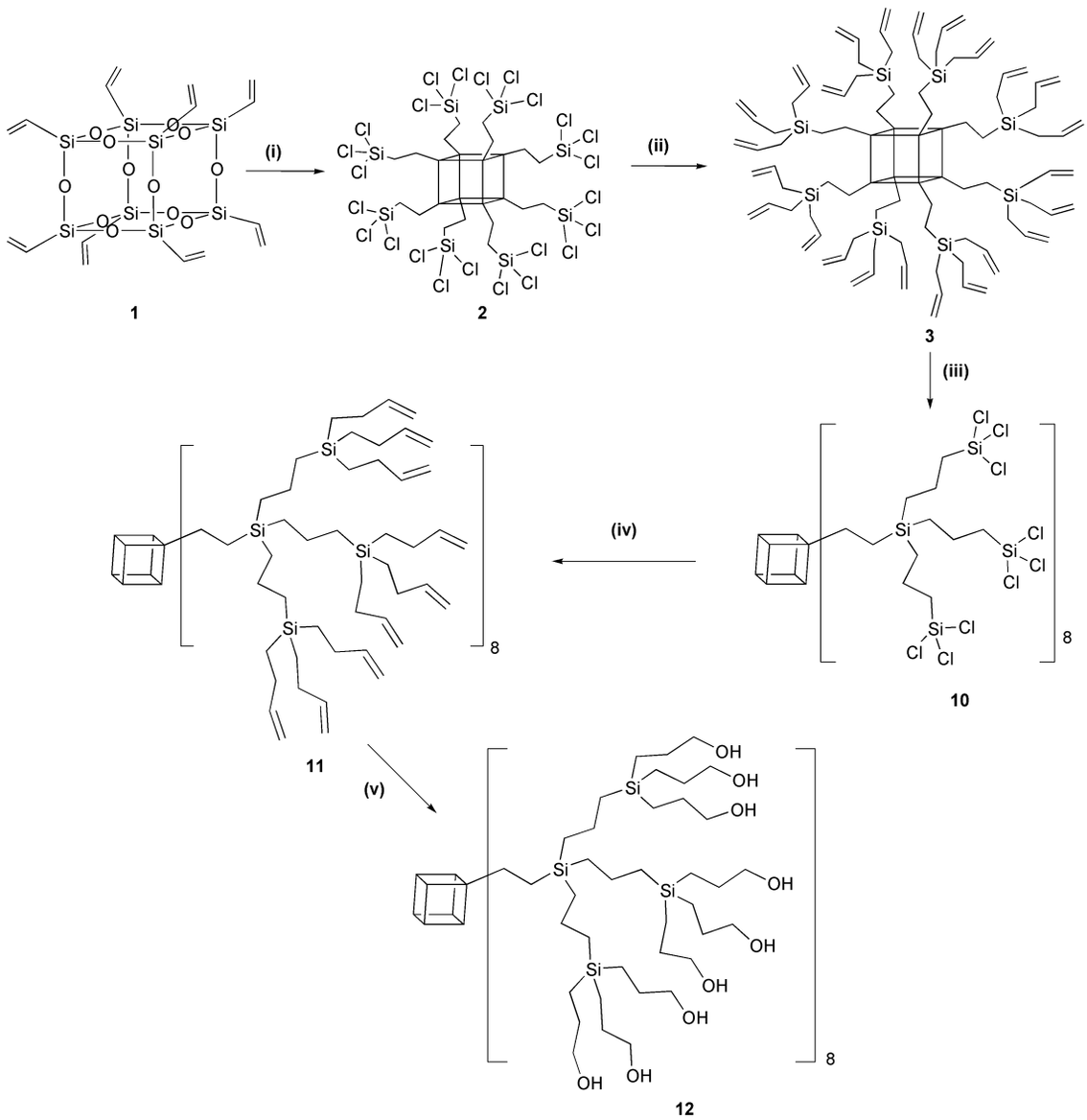


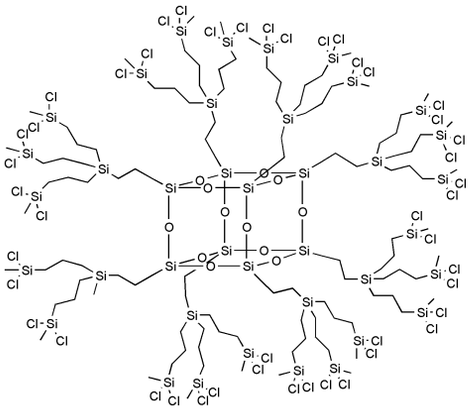
Scheme 1 Synthesis of POSS-72OH. For clarity, Si–O–Si linkages in the POSS core are shown as lines connecting the two silicon atoms and only one dendrimer branch is shown for the larger molecules. See Experimental section for reagents and conditions.

Results and discussion

The preparation of the dendrimers was accomplished according to Scheme 1. Octavinylsilsesquioxane (**1**) was prepared according to the standard literature methods by the careful hydrolysis of vinyltrichlorosilane.[11] Hydrosilation using trichlorosilane ($HSiCl_3$) and Speier's catalyst (H_2PtCl_6) quantitatively and regioselectively under rigorously dry conditions adds eight trichlorosilyl units to the terminal (α) carbons of the dendrimer to form the 1st generation POSS-24Cl (**2**).

The POSS-24Cl dendrimer can react with vinylmagnesium bromide to give a 24 vinyl dendrimer, as has been reported previously.[5] However, POSS-24Cl also reacts with allylmagnesium bromide to give a 24 allyl dendrimer, POSS-24Allyl (**3**) in a similar manner to that shown in other carbosilane dendrimer preparations.[12] This allylation reaction again occurs almost quantitatively and once recovered from solution, the purity was sufficient (as shown by ^{1}H NMR, ^{13}C NMR and CHN microanalysis) to be used in subsequent reactions without any further purification. The POSS-24Allyl dendrimer (**3**) was hydrosilated by trichlorosilane to give the POSS-72Cl dendrimer (**10**). In this case, the hydrosilation is more effectively catalysed by Karstedt's catalyst (a platinum divinylsiloxane complex), allowing the reaction to be completed at or below room temperature. This has some important implications for the regioselectivity of the hydrosilation (see below). After stirring at room temperature for 48 hours, ^{1}H NMR showed that there were no residual allylic double bonds remaining on the dendrimers, indicating that the reaction had gone to completion. Purification and characterization of this dendrimer was not easy, because it is difficult to remove all the solvent (THF) from the product, presumably because some solvent molecules are effectively trapped by the longer arms of the second generation dendrimer. This is a common problem in many high generation dendrimer syntheses. After almost all trichlorosilane and THF were removed, the POSS-72Cl (**10**) was reacted with excess allylmagnesium bromide to give another allylic end dendrimer, POSS-72Allyl (**11**). ^{13}C NMR clearly showed that in the hydrosilation of POSS-24Allyl by trichlorosilane, silicon was only connected to the α-carbon atoms of the allyl groups. This is consistent with previous work on hydrosilation reactions, which shows that reaction at low temperature, as was the case here, leads to addition exclusively at the α-carbon.[13]

Hydroboration of POSS-72Allyl (**11**) using 9-BBN (9-borabicyclo[3.3.1]nonane) led to anti-Markovnikov addition of boron at double bonds. Oxidation of the prepared dendritic borane dendrimer in basic medium produced hydroxyl-terminated dendrimers, POSS-72OH (**12**). Again, ^{13}C NMR, together with CHN microanalysis, indicated that this reaction



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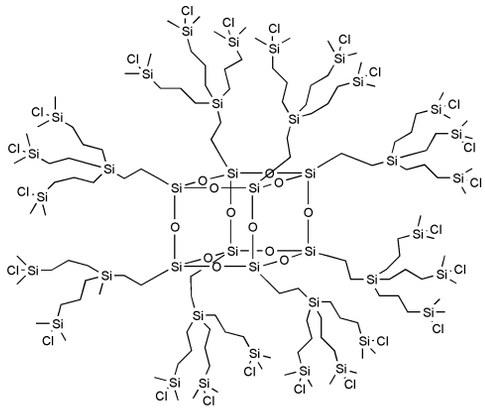

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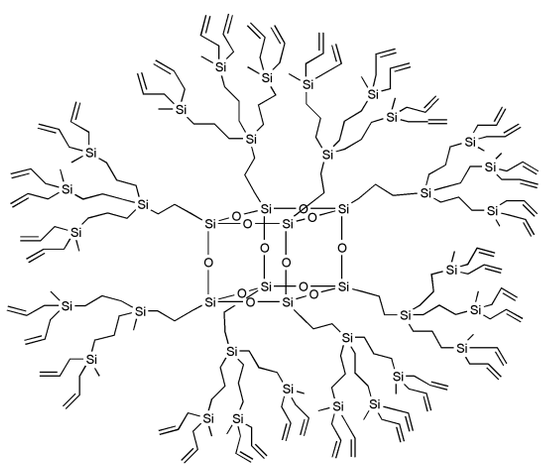

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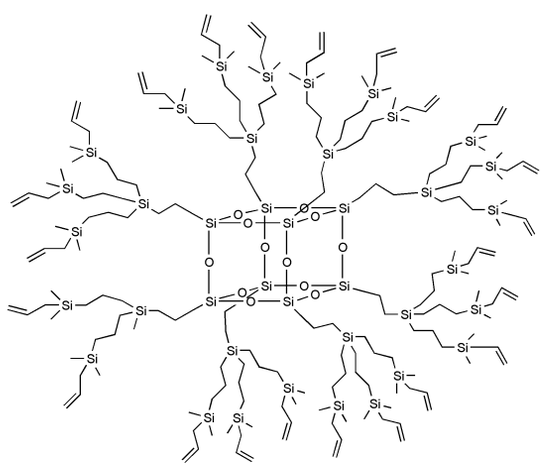

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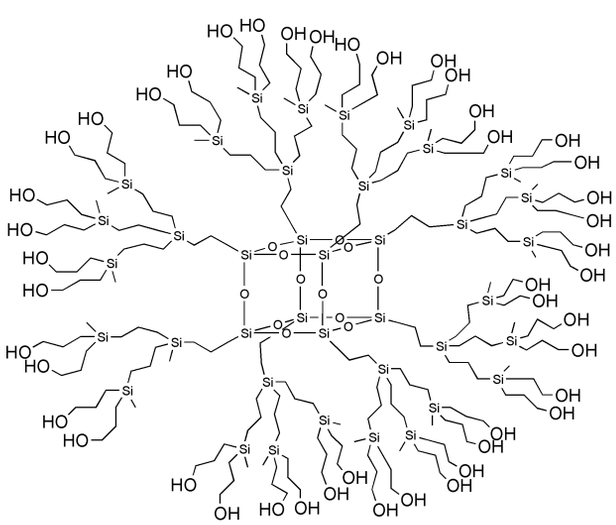

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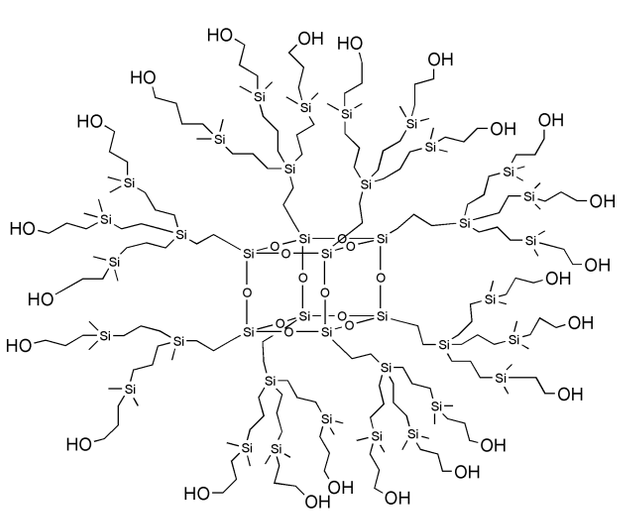

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had gone in high yield to give an 'ideal' (*i.e.* all functionalisation at the α-carbon) dendrimer.

Through similar processes, POSS-24Cl48Me (**7**), POSS-24Allyl48Me (**8**), POSS-24OH48Me (**9**), POSS-48Cl24Me (**4**), POSS-48Allyl24Me (**5**) and POSS-48OH24Me (**6**) were also successfully prepared. However, the optimum reaction conditions needed to prepare these dendrimers are not always the same as those indicated above. The first important difference is the different reaction temperatures for the hydrosilation of POSS-24Allyl by chlorodimethylsilane, dichloromethylsilane and trichlorosilane. This is the most important step for the building of allyl terminated dendrimers, because in the hydrosilation silicon can be connected to α- (terminal) or the β-carbon atom of the allylic group. The reaction temperatures and reaction time for the hydrosilation of the POSS-24allyl dendrimer with trichlorosilane, dichloromethylsilane and chlorodimethylsilane were carefully examined in order to obtain dendrimers with the silicon regioselectively attached to the terminal carbon of the dendrimer.

This regioselectivity of the hydrosilation reaction can be most easily determined *via* ^{13}C NMR. If there were a significant proportion of silation at the β carbon, ^{13}C NMR would result in a more complex spectrum of the resultant dendrimer than would be the case for the more symmetric 'ideal' structure. After many reactions, the optimum reaction conditions for the hydrosilation reactions were as follows. For chlorodimethyl-

silane, hydrosilation can only be completed by heating the mixture (diethyl ether as solvent) at reflux. Hydrosilation at room temperature was not complete after 48 hours, ^{1}H NMR revealing the presence of unreacted allylic double bonds. In the case of dichloromethylsilane, hydrosilation went to completion very quickly at reflux, but the ^{13}C NMR indicated a significant amount of β-addition in the product dendrimer. At room temperature the reaction was complete within 48 hours, and the NMR analysis indicated that the resultant POSS-48Allyl24Me dendrimers contained no β-addition products. For trichlorosilane, room temperature is still too high for the formation of the ideal structure, β-addition products were clearly visible in the ^{13}C NMR spectra. The reaction temperature was reduced to 0 °C for 24 hours and then allowed to come up to room temperature for 24 hours. In this case no β-addition resonances were visible in the spectra.

These results illustrate two general features of the hydrosilation reactions in dendrimers. Firstly, steric influences are important in determining both the rate and regioselectivity of the reactions, and secondly that the temperature is important in determining the regioselectivity. In general, it is difficult to hydrosilate unhindered allylsilanes in a regioselective manner. This is presumably because of the so-called β-effect in silicon chemistry. This would tend to promote addition at the β-position in allylsilanes, instead of addition at the (usually more favoured) α-position. Note that in vinylsilanes, the effect of the silicon would be expected to promote hydrosilation at the α-carbon of the vinyl group, thereby increasing the regioselectivity of the reaction. This is indeed the case, illustrated by the fact that it is relatively easy to hydrosilate octavinylsilsesquioxane **1** in a regioselective manner.

In allyl-terminated dendrimers, especially those where the density of terminal double bonds is high, as is the case for the 2nd generation POSS-based dendrimers described here, β-addition would be more sterically demanding than α-addition. That decreasing the temperature of the reaction also increases the regioselectivity of the reaction is reasonably well known and is a useful tool in syntheses of this kind.[8,13]

The hydroboration and subsequent oxidation reactions to produce the hydroxy-terminated dendrimers also occur in a regioselective manner, with α-addition being favoured. The dendrimers produced in this way show some interesting solubility properties, being easily dissolved in alcohols, such as ethanol, and DMSO but relatively insoluble in most other solvents.

The characterisation and structural determination of dendrimers is complex due to the large size and high symmetry of the molecules. Many potential applications for dendritic species may depend on the conformation of the molecule in solution and so it is vital that we have methods of measuring or predicting the conformations. Atomistic molecular modelling provides one way in which we can predict possible low energy conformations. Of particular relevance to our work on potential catalytic supports, we are interested in where the terminal groups are located.

The primary structure of dendrimers has been of great interest and determination of certain characteristics of many families of dendritic molecules has been attempted using various theoretical methods. Work by various groups using non-atomistic methods predicted that the terminal groups of the dendrimer were not always located at the exterior of the molecule. Lescanec and Muthukumar,[14] using a kinetic growth model showed that there was a decrease in density on going from the centre to the periphery and that the ends of the branches did fold backwards into the dendritic interior. Such findings have also been corroborated by Murat and Grest,[15] Mansfield and Klushin,[16] and Boris and Rubinstein[17] using various theoretical models. Generally it has been found that the significance of back folding and indeed the extent to which it occurs depends largely on the generation of the dendrimer and the composition of the branch. If a longer, more flexible monomer unit is used, more back folding may be observed.

Atomistic simulations have more recently been used by several groups to determine dendrimer properties. Naidoo *et al.*[18] investigated the structure and conformation of organic and organochromium poly(benzylphenyl ether) dendrimers with a view to their potential use as catalytic supports. It was found that while the metal carbonyl species present were available to take part in chemical reactions, the terminal groups of both types of dendrimers smaller than generation three underwent significant back folding and penetrated the core region. In the case of organochromium dendrimers larger than the third generation, the terminal groups do not penetrate the core to the same extent. This is thought to be due to the large size of the chromium terminal groups as similar trends were not observed for the purely organic dendrimer.

Cavallo and Fraternali[19] reported the results of a molecular dynamics study of the first five generations of poly(propylene imine) with *N*-t-Boc-L-phenylalanine terminal units. It was found that the shape of the dendrimer was generation dependent with higher generations becoming more spherical. Some back folding of the terminal groups into the interior was also observed. Gorman and Smith[20] reported the effects of monomer flexibility on overall dendrimer configuration. While it was found that dendrimers constructed of flexible monomers were more globular in shape, all dendrimers gave distributions of terminal groups throughout the molecules thought to be due to back folding in the former case and branching angle effects in the latter.

Our hypothesis was that a rather bulky, high multiplicity core such as a POSS molecule, should lead to relatively spherical (or globular) dendrimers even at low generation number. Results from the molecular dynamics production runs on the 24-, 48- and 72-hydroxy functionalised dendrimers indicate that, in general, this hypothesis is borne out.

Molecular dynamics simulations, using the Materials Studio Software from MSI Inc. were carried out using both 'good' and 'poor' solvent protocols, including terms for both coulombic and van der Waals interactions and only van der Waals respectively.[21] The models recovered from both types of solvent quality dynamics reveal fairly globular dendrimers with the majority of the oxygen atoms in each case available at the surface of the molecules (Fig. 1). The calculation of the aspect ratios of the dendrimers I_z/I_x and I_z/I_y, where I_x, I_y, and I_z are the principal moments of inertia of the molecules with respect to directions x, y and z respectively ($I_z > I_y > I_z$) (Table 1), indicate that the molecules are relatively spherical. The maximum calculated aspect ratio for any dendrimer studied was ≈1.2 and there is no correlation of aspect ratios with the number of terminal groups on the dendrimer, nor with solvent type. This is especially interesting when one compares the results of molecular dynamics simulations on 2nd generation dendrimers based on cores of lower multiplicity. For example, Gorman and Smith,[20] and Cavallo and Fraternali[19] report aspect ratios significantly larger than those reported here (>2) even for fourth and fifth generation dendrimers. This is presumably a consequence of the three-dimensional nature of the POSS core, which is simply amplified by addition of dendrimer branches at all vertices of the cube.

However, close inspection of the average positions of the oxygen atoms over the course of the production dynamics run, indicates that by no means all the oxygen atoms are distributed at the surface of the dendrimer. Calculating the radial distribution functions as a sum over the whole production dynamics for the terminal groups on one branch and the silicon atom of the core that generates the branch shows that the terminal groups are not uniformly distributed on the exterior surface of the dendrimer (Fig. 2). For all three cases the terminal –OH groups are distributed in a shell between 6 and 13.5 Å from the silicon of the POSS to which the branch containing the terminal

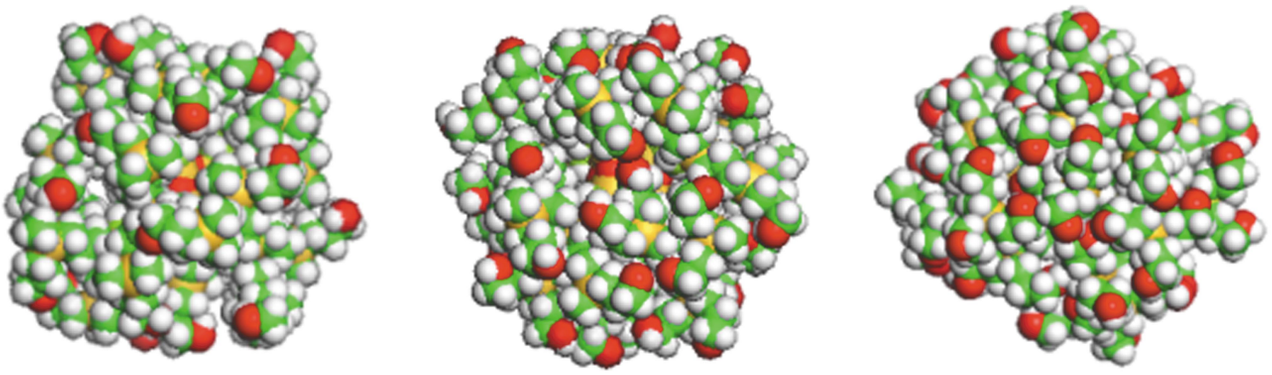

Fig. 1 Space filling models of the POSS-24OH48Me (left), POSS-48OH24Me (centre) and POSS-72OH (right) dendrimers. The majority of the oxygen atoms are on the external surface of the molecule. (Key: C = green, Si = yellow, O = red, H = white).

Table 1 Aspect ratios (calculated from moments of inertia (I_i, relative to orthogonal axes x, y and z), and radii of gyration (R_g) for POSS-24OH48Me, POSS-48OH24Me and POSS-72OH dendrimers calculated from the molecular dynamics results using both 'good' and 'poor' solvent protocols

Dendrimer	Solvent	I_z/I_x	I_z/I_y	R_g/Å
POSS-24OH48Me	Good	1.03	1.02	9.65
	Poor	1.08	1.01	9.70
POSS-48OH24Me	Good	1.20	1.03	10.32
	Poor	1.18	1.15	10.03
POSS-72OH	Good	1.26	1.16	10.80
	Poor	1.15	1.01	10.88

groups is attached. This means the oxygen atoms are distributed in a shell between ≈8.5 Å and ≈16 Å away from the centre of mass of the dendrimer. In the POSS-24OH48Me dendrimer (**9**), all the terminal oxygen atoms lie within this shell. For the POSS-48OH24Me (**6**) and POSS-72OH (**12**) dendrimers a small proportion of the terminal hydroxypropyl groups back fold in towards the centre of the dendrimer, coming as close as ≈3 Å to the POSS silicon atoms and possibly close enough to form hydrogen bonds with the oxygen atoms in the POSS cores. Presumably this is due to the greater steric bulk at the surface as methyl groups are replaced by hydroxypropyl units, which forces a small proportion of the terminal hydroxypropyl groups inwards. The number of back folded branches increases as the number of terminal hydroxypropyl groups increases, as would be expected.

The distribution of terminal OH · · · OH distances in the dendrimer is less dependent on the number of terminal hydroxypropyl groups (Fig. 3). The increase in steric bulk at the surface does not force the –OH groups closer together to any significant extent, but rather back folding of the branches occurs to release any steric congestion. Qualitatively, the distributions look very similar for all three dendrimers, with a number of short hydrogen bonding distances and a distribution of longer distances. There is a maximum in $g(r)$ in all three cases at ≈9 Å, which seems to correlate with the OH · · · OH distance between hydroxyls on the same dendrimer branch, separated by a 15 atom spacer ($HO–(CH_2)_3Si(CH_2)_3Si(CH_2)_3Si(CH_2)_3–OH$), which is present in all three dendrimers. The dynamics also indicate that there is no mixing or entanglement of the branches in the dendrimers (Fig. 4).

Conclusions

Divergent synthetic methods have been used to prepare a number of novel POSS-based dendrimers. The optimum conditions for the synthesis have been identified and molecular modelling studies have shown the resulting molecules to have low energy conformations yielding relatively spherical structures with the

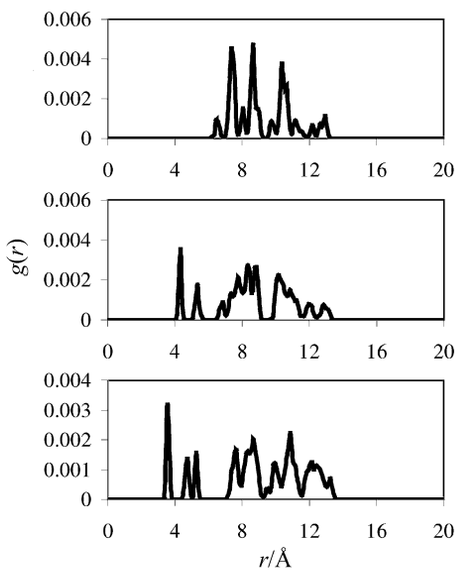

Fig. 2 Radial distribution functions for POSS-24OH48Me (top), POSS-48OH24Me (middle) and POSS-72OH (bottom) showing the distance between the terminal hydroxy groups and the core of the dendrimer. These distributions were calculated from the results of the molecular dynamics using the 'good' solvent protocol.

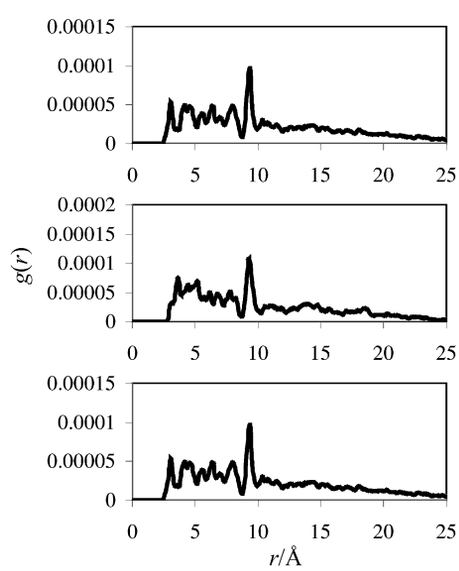

Fig. 3 Radial distribution functions showing the distances between terminal hydroxy groups for POSS-24OH48Me (top), POSS-48OH24Me (middle) and POSS-72OH (bottom). These distributions were calculated from the results of the molecular dynamics using the 'good' solvent protocol.

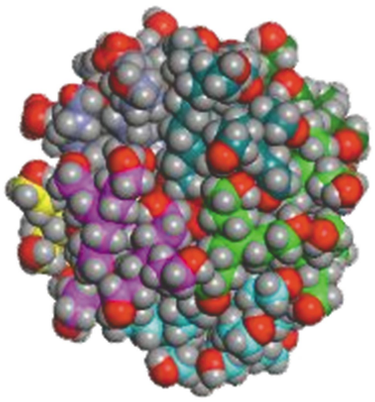

Fig. 4 Space filling model of POSS-72OH with each dendrimer branch displayed using a different colour (oxygen atoms of the hydroxy groups are all shown in red and hydrogen atoms in grey). This shows there is very little mixing of the dendrimer branches.

majority of the terminal groups on the exterior surface of the molecule. However, the degree of back folding of dendrimer branches is shown to be dependent on the number of terminal groups.

Experimental

Synthesis of dendrimers

All manipulations dealing with air and/or moisture sensitive compounds were carried out under an atmosphere of nitrogen. Solvents were dried according to established procedures. ^{1}H NMR spectra were recorded at 300.13 MHz, ^{13}C NMR spectra at 75.47 MHz and ^{29}Si NMR spectra at 59.63 MHz on a Bruker AM300 spectrometer operating in the Fourier transform mode with, for ^{13}C spectra, noise proton decoupling. Chemical analysis was by the University of St. Andrews Microanalysis service. Preparation of **1** and **2** given in ref. 5.

1,3,5,7,9,11,13,15-Octakis(2-(allylsilyl)ethyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-24Allyl) 3. Allylmagnesium bromide (Aldrich, 1.0 mol dm^{-3} in diethyl ether, 50 ml, 0.05 mol) was dropped slowly into a solution of POSS-24Cl (2.40 g, 1.4 mmol) in diethyl ether (25 ml) and tetrahydrofuran (25 ml) with strong stirring at room temperature. The resulting solution was stirred at room temperature for 24 h. The mixture was then added slowly to an ice-cooled saturated aqueous solution of ammonium chloride (100 ml). The water phase was extracted with hexane (2 × 100 ml). The combined organic layers were washed with brine, dried over Mg_2SO_4 and concentrated *in vacuo*. The residue was a viscous colourless oil (2.46 g, 95%). ^{1}H NMR and ^{13}C NMR showed that there were almost no byproducts. POSS-24Allyl was used for further reaction without purification. Microanalysis found C, 56.6; H, 8.7; $Si_{16}O_{12}C_{88}H_{152}$ requires C, 57.1; H, 8.3%. ^{1}H NMR ($CDCl_3$): δ 5.8 (C*H*=CH$_2$, 3H), 4.9 (CH=C*H*$_2$, 6H), 1.6 (C*H*$_2$CH=CH$_2$, 6H), 0.63 (C*H*$_2$C*H*$_2$, 4H). ^{13}C NMR ($CDCl_3$): δ 134.5 (*C*H=CH$_2$), 113.4 (CH=*C*H$_2$), 19.2 (Si*C*H$_2$CH=CH$_2$), 4.4 (OSi*C*H$_2$CH$_2$), 2.9 (OSiCH$_2$*C*H$_2$).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(methyldichlorosilyl)-propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-48Cl24Me) 4. POSS-24Allyl (4.0 g, 2.16 mmol), dichloromethylsilane (30 ml, 0.29 mol) and THF (100 ml) were added into a 250 cm^3 flask, and then Karstedt catalyst (Aldrich, 40 drops) in xylene solution was added into the above solution. The mixture was stirred at room temperature for 48 hours. ^{1}H NMR showed that there was no carbon double bond left. Most solvent was removed *in vacuo* to give a white solid.

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(methyldiallylsilyl)-propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-48Allyl24Me) 5. Allylmagnesium bromide (Aldrich, 1.0 mol dm^{-3} in diethyl ether, 150 ml) was added slowly to a solution of POSS-48Cl24Me (9.9 g, 2.15 mmol) in diethyl ether (75 ml) and tetrahydrofuran (75 ml) with strong stirring at room temperature. The resulting mixture was stirred at room temperature for 24 h. The mixture was stirred intensely and added slowly into an ice-cooled saturated solution of ammonium chloride (200 ml). The water phase was extracted with hexane (2 × 100 ml). The combined organic layers were washed with brine, dried over Mg_2SO_4 and concentrated *in vacuo*. The residue was loaded on a column of silica gel and eluted with hexane to yield POSS-48Allyl24Me as a colorless viscous oil (6.8 g, 65%). Microanalysis found C, 63.0; H, 10.0; $Si_{16}O_{12}C_{88}H_{152}$ requires C, 63.0; H, 10.1%. ^{1}H NMR ($CDCl_3$): δ 5.77 (C*H*=CH$_2$, 6H), 4.88 (CH=C*H*$_2$, 12H), 1.56 (SiC*H*$_2$CH=CH$_2$, 12H), 1.36 (CH$_2$C*H*$_2$CH$_2$, 6H), 0.60 (OSiC*H*$_2$C*H*$_2$, C*H*$_2$CH$_2$C*H*$_2$, 16H), 0.00 (Si(C*H*$_3$), 9H). ^{13}C NMR ($CDCl_3$): δ 134.8 (*C*H=CH$_2$), 113.6 (CH=*C*H$_2$), 21.7 (*C*H$_2$CH=CH$_2$), 18.7, 18.5, 17.2 (*C*H$_2$-*C*H$_2$*C*H$_2$), 4.8~4.6 (OSi*C*H$_2$*C*H$_2$), −5.4 (SiCH$_3$). ^{29}Si NMR: δ −66.60 (OSi), 0.14 (SiCH$_2$CH=CH$_2$), 2.71 (OSiCH$_2$CH$_2$*Si*).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(bis(3-hydroxypropyl)-methylsilyl)propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (POSS-48OH24Me) 6. POSS-48Allyl24Me (2.0 g, 0.41 mmol) and THF (90 cm^3) were added into a 500 cm^3 flask. The solution was cooled to −10 °C and then 9-BBN (4.8 g in 90 cm^3 THF) was dropped slowly into the above cold solution. The mixture was stirred at −10 °C for 3 hours and at room temperature for 24 hours. ^{1}H NMR showed that no hydrogens of the double bonds were left. The solution was cooled to −10 °C again. A mixture of NaOH (1.57 g in 6.5 cm^3 water) and H_2O_2 (11.0 ml) was added slowly into the above cooled solution. The resulting mixture was stirred at −10 °C for one hour, and then warmed to room temperature, and finally heated to 50 °C for 3 hours. After being cooled to room temperature, the THF solution was decanted from the precipitated boric acid and the aqueous medium. THF was removed from the solution and the residual colorless liquid was loaded on a column of silica gel and eluted with THF and ethanol to yield POSS-48OH24Me as a colorless solid (1.41 g, 60%). Microanalysis found C, 55.1; H, 10.2; $Si_{40}O_{60}C_{256}H_{584}$ requires C, 53.5; H, 10.2%. ^{1}H NMR (DMSO): δ 4.32 (CH$_2$O*H*, 6H), 3.33 (CH$_2$C*H*$_2$OH, 12H), 1.36 (CH$_2$C*H*$_2$CH$_2$, 18H), 0.50 (SiCH$_2$, 28H), −0.06 (Si(CH$_3$)$_2$, 9H). ^{13}C NMR (DMSO): δ 63.9 (CH$_2$OH), 26.8 (*C*H$_2$CH$_2$OH), 9.31 (*C*H$_2$CH$_2$CH$_2$OH), 18.1–16.4 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 3.8 (OSi-*C*H$_2$*C*H$_2$), −5.3 (SiCH$_3$). ^{29}Si NMR (Ethanol): δ −66.29 (OSi), 3.41 (SiCH$_2$CH$_2$CH$_2$OH), 3.00 (OSiCH$_2$CH$_2$*Si*).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(chlorodimethylsilyl)-propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-24Cl48Me) 7. POSS-24Allyl (4.0 g, 2.16 mmol), chlorodimethylsilane (30 ml, 0.27 mol), 100 cm^3 diethyl ether and H_2PtCl_6 (45 drops, 0.1 mol dm^{-3} in isopropanol) were added into a 250 cm^3 flask. The resulting solution was refluxed for 48 hours. ^{1}H NMR showed that there was no double bond left. The solvent was removed *in vacuo* to give POSS-24Cl48Me as a colorless sticky oil. ^{13}C NMR ($CDCl_3$): δ 23.8, 18.6, 16.3 (*C*H$_2$*C*H$_2$*C*H$_2$), 4.7, 4.2 (OSi*C*H$_2$*C*H$_2$), 2.2 (Si(CH$_3$)$_2$).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(allyldimethylsilyl)-propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-24Allyl48Me) 8. Allylmagnesium bromide (Aldrich, 1.0 M in diethyl ether, 77 ml) was added slowly to a solution of POSS-24Cl48Me (8.9 g) in diethyl ether (80 ml) with intense stirring at room temperature. The resulting mixture was stirred at room temperature for another 24 hours. The mixture was stirred intensely and added slowly into an ice-cooled saturated solution of ammonium chloride (100 ml). The water phase was

extracted with hexane (2 × 50 ml). The combined organic layers were washed with brine, dried over Mg_2SO_4 and concentrated *in vacuo*. The residue was loaded on a column of silica gel and eluted with hexane to yield POSS-24Allyl48Me as a colorless viscous oil (7.3 g, 80%). Microanalysis found C, 59.8; H, 10.7; $Si_{16}O_{12}C_{88}H_{152}$ requires C, 58.7; H, 10.4%. ^{1}H NMR ($CDCl_3$): δ 5.80 (C*H*=CH_2, 3H), 4.86 (CH=C*H*$_2$, 6H), 1.53 (SiC*H*$_2$CH=CH_2, 6H), 1.36 ($CH_2CH_2CH_2$, 6H), 0.60 (OSiC*H*$_2$C*H*$_2$, C*H*$_2$CH$_2$C*H*$_2$, 16H), 0.00 ($Si(CH_3)_2$, 36H). ^{13}C NMR ($CDCl_3$): δ 135.3 (*C*H=CH_2), 112.9 (CH=*C*H$_2$), 20.1 (Si*C*H$_2$CH=CH_2), 19.9, 18.7, 17.0 (*C*H$_2$*C*H$_2$*C*H$_2$), 4.8 (OSi*C*H$_2$*C*H$_2$), −3.4 ($SiCH_3$). ^{29}Si NMR: δ −66.53 (OSi), 0.62 ($SiCH_2CH=CH_2$), 2.83 ($OSiCH_2CH_2$*Si*).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(3-hydroxypropyl)-(dimethylsilyl)propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (POSS-24OH48Me) 9. POSS-24Allyl48Me (2.0 g, 0.47 mmol) and 50 cm^3 THF were added into a 250 cm^3 flask. The solution was cooled to −10 °C and then 9-BBN (2.8 g in 50 cm^3 THF solution) was dropped slowly into the cooled solution. The resulting solution was stirred at −10 °C for 3 hours and at room temperature overnight. ^{1}H NMR showed that no hydrogens of double bonds were left. The solution was cooled to −10 °C again. A mixture of NaOH (0.9 g in 3.8 cm^3 water) and H_2O_2 (6.4 cm^3) was added slowly into the above cooled solution. The resulting mixture was stirred at −10 °C for one hour, and then warmed to room temperature, and finally heated to 50 °C for 3 hours. After being cooled to room temperature, the THF solution was decanted from the precipitated boric acid and the aqueous medium. THF was removed from the solution and the residual colorless liquid was loaded on a column of silica gel and eluted with ethyl acetate and ethanol to yield POSS-24OH48Me as a colorless viscous oil (1.76 g, 80%). Microanalysis found C, 54.2; H, 11.0; $Si_{40}O_{36}C_{208}H_{488}$ requires C, 53.3; H, 10.5%. ^{1}H NMR (DMSO): δ 4.30 (CH_2OH, 3H), 3.33 (C*H*$_2$OH, 6H), 1.37 ($CH_2CH_2CH_2$, 12H), 0.50 ($SiCH_2$, 22H), 0.00 ($Si(CH_3)_2$, 18H). ^{13}C NMR (DMSO): δ 63.8 (CH_2OH), 26.8 (*C*H$_2$CH$_2$OH), 10.7 (*C*H$_2$CH$_2$CH$_2$OH), 19.5, 17.9, 16.3 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 3.8 (OSi*C*H$_2$*C*H$_2$), −3.5 ($SiCH_3$). ^{29}Si NMR (Ethanol): δ −66.29 (OSi), 2.19 ($SiCH_2$-CH_2CH_2OH), 3.08 ($OSiCH_2CH_2$*Si*).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(trichlorosilyl)propyl)-silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-72Cl) 10. POSS-24Allyl (4.0 g, 2.16 mmol), THF (200 ml) and trichlorosilane (30 ml, 0.30 mol) were added into a 500 cm^3 flask. The resulting solution was cooled by ice bath for one hour, and then Karstedt catalyst (40 drops) in xylene solution was added. The mixture was stirred in an ice bath for 24 hours and then warmed slowly to room temperature and stirred at room temperature for another 48 hours. ^{1}H NMR showed that there were no double bonds left. Most of the THF was removed *in vacuo* to give POSS-72Cl as a white solid.

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(triallylsilyl)propyl)silyl)-ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-72Allyl) 11. Allylmagnesium bromide (Aldrich, 1.0 mol dm^{-3} in diethyl ether, 233 cm^3, 0.23 mol) was added slowly to a solution of POSS-72Cl (11.0 g, 2.16 mmol) in diethyl ether (100 cm^3) and tetrahydrofuran (100 cm^3) with strong stirring at room temperature. The resulting mixture was stirred at room temperature for 24 h. The mixture was stirred intensely and added slowly into an ice-cooled saturated solution of ammonium chloride (200 cm^3). The water phase was extracted with hexane (2 × 200 ml). The combined organic layers were washed with brine, dried over Mg_2SO_4 and concentrated *in vacuo*. The residue was loaded on a column of silica gel and eluted with hexane to yield POSS-72Allyl as a colorless viscous oil (7.12 g, 60%). Microanalysis found C, 66.36; H, 9.87; $Si_{40}O_{12}C_{304}H_{536}$ requires C, 66.30; H, 9.81%. ^{1}H NMR ($CDCl_3$): δ 5.77 (C*H*=CH_2, 9H), 4.90 (CH=C*H*$_2$, 18H), 1.60 (SiC*H*$_2$CH=CH_2, 18H), 1.39 ($CH_2CH_2CH_2$, 6H), 0.67 (OSiC*H*$_2$C*H*$_2$, C*H*$_2$CH$_2$C*H*$_2$, 16H). ^{13}C NMR ($CDCl_3$): δ 134.5 (*C*H=CH_2), 113.9 (CH=*C*H$_2$), 19.9 (*C*H$_2$CH=CH_2), 18.6, 17.3, 17.0 (*C*H$_2$*C*H$_2$*C*H$_2$), 4.8~4.6 (OSi*C*H$_2$*C*H$_2$). ^{29}Si NMR: δ −66.62 (OSi), −1.17 ($SiCH_2CH=CH_2$), 2.62 ($OSiCH_2CH_2$*Si*).

1,3,5,7,9,11,13,15-Octakis(2-(tris(3-(tris(3-hydroxypropyl)-silyl)propyl)silyl)ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS-72OH) 12. POSS-72Allyl (2.0 g, 0.36 mmol) and 120 cm^3 THF were added into 500 cm^3 flask. The solution was cooled to −10 °C and then 9-BBN (6.3 g in 120 cm^3 of THF solution) was added slowly. The solution was stirred at −10 °C for 3 hours and at room temperature for 48 hours. The solution was cooled to −10 °C again. A mixture of NaOH (2.1 g in 7.4 cm^3 water) and H_2O_2 (12.4 ml) was added slowly into the above cooled solution. The resulting mixture was stirred at −10 °C for one hour and warmed to room temperature and heated at 50 °C for 3 hours. After being cooled to room temperature, the THF solution was decanted from the precipitated boric acid and the aqueous medium. The THF was removed from the solution and the residual colorless liquid was loaded onto a column of silica gel and eluted with a mixture of THF–ethanol (5% ethanol) and then with ethanol to yield POSS-72OH as a colorless solid (1.97 g, 80%). Microanalysis found C, 56.1; H, 9.8; $Si_{40}O_{84}C_{304}H_{680}$ requires C, 53.7; H, 10.1%. ^{1}H NMR (DMSO): δ 4.3 (CH_2OH, 9H), 3.3 (CH_2CH_2OH, 18H), 1.3 ($CH_2CH_2CH_2$, 24H), 0.5 ($SiCH_2$, 34H). ^{13}C NMR (DMSO): δ 63.9 (CH_2OH), 26.8 (*C*H$_2$CH$_2$OH), 7.8 (*C*H$_2$CH$_2$CH$_2$OH), 18.0~16.0 (Si*C*H$_2$-*C*H$_2$*C*H$_2$Si), 3.8 (OSi*C*H$_2$*C*H$_2$). ^{29}Si NMR (Ethanol): δ −66.2 (OSi), 4.1 ($SiCH_2CH=CH_2$), 2.8 ($OSiCH_2CH_2$*Si*).

Molecular modelling

Molecular modelling was carried out using the Discover program contained in the Insight (II) Molecular Modelling Suite of Molecular Simulations Inc.[21]

Molecular dynamics were performed using the consistent valence force field (CVFF), containing the following potential terms:

$$E_{\text{pot}} = \sum_b H_b(b-b_0)^2 + \sum_\theta H_\theta(\theta-\theta_c)^2 + \sum_\phi H_\phi[1+\cos(n\phi)] + \sum_\chi H_\chi\chi^2 + \sum\varepsilon\left[\left(r^*/r\right)^{12} - 2\left(r^*/r\right)^6\right] + \sum q_i q_j/\varepsilon r_{ij} \quad (1)$$

The potential energy is given in terms of the bond stretch term (b), the valence angle term (θ), the torsional potential (φ), the Wilson out of plane potential (χ), a 12–6 potential describing the non-bonded interactions and a coulombic potential. Force field parameters were taken directly from the CVFF force field supplied with Materials Studio. No cross terms were taken into account.

The force field parameters were altered to represent the cases of a good and poor solvent. CVFF (good) represented a good solvent by only considering the repulsive van der Waals forces between non-bonded atoms. CVFF (poor) was used to represent a poor solvent by considering both Coulombic and van der Waals forces between non-bonded atoms. The dendrimers were drawn using the draw facility on the Materials Studio viewer and minimized using steepest descent/conjugate gradient methods to a maximum energy derivative of less than RMS 0.001 kcal mol^{-1} Å^{-1}, relaxing bond lengths to their equilibrium distances. The models were then subjected to the heating and annealing process designed to reach a global minimum of energy for the structure. The structures were first heated to 1000 K to facilitate full expansion of the branches with a time step of 1 fs, and then annealed by reducing the temperature in 50 K steps for 5 ps dynamics down to 50 K. At 50 K the structures were again minimized to a maximum energy

derivative of less than 0.001 kcal mol^{-1} $Å^{-1}$ and allowed to equilibrate at 273 K for 600 ps. Every 1000th configuration of the structure was saved in full for analysis. The final 500 ps (500 frames) of the equilibration trajectory was used for analysis.

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