Synthesis of functional cubes from octavinylsilsesquioxane (OVS)

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Octavinylsilsesquioxane, $(CH_2CH)_8Si_8O_{12}$, a cubic molecule with vinyl groups at each vertex, has been elaborated to give a series of potential starting materials for nanohybrid synthesis. Terminal bromophenyl groups were introduced onto the surface of octavinylsilsesquioxane either by cross-metathesis or hydrosilylation to give fully bromide substituted **POSS A**, **POSS B** and **POSS C**; the last two were further capped with trimethylsilylacetylene by Sonogashira coupling to produce **POSS D** and **POSS E**, showing interesting potential for more useful end group functionalisation. Heck coupling with iodobenzene was used to make the simple phenyl terminated dendrimer **POSS F**. Cross-metathesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene with octavinylsilsesquioxane afforded **POSS G** with eight aryl borate groups on its periphery, suitable for use as a starting material in Suzuki coupling. Finally, **POSS H** has been functionalized with 8 benzyl chloride groups *via* Grubbs coupling, allowing further substitutions by nucleophiles.

Introduction

Dendrimers are perfect monodisperse macromolecules with three-dimensional architecture, which have a central core with a number of branching dendron units attached. Their construction typically involves stepwise repetitive reaction sequences in the divergent approach[1] or convergent methodology.[2] It is possible to tune the structure, size, shape and solubility of these dendrimers to give persistent, controllable dimensions (1–100 nm) and topologies with specific functionalities in predetermined positions. As a result, the development of different synthetic approaches, which lead to ever more complex dendrimers[3] and various practical uses including biological applications,[4] catalysis,[5,6] light emitting materials,[7,8] are currently under investigations.

Dendritic macromolecules based on polyhedral oligomeric silsesquioxanes (POSS) cores have been synthesized and widely used in materials chemistry applications ranging from models of silica surfaces[9] and zeolites[10] to organic-inorganic hybrid polymers.[11,12] A standard method of preparation of these latter nanomaterials is the substitution of one or more of the POSS corner groups by a functional moiety X capable of undergoing polymerization, followed by its incorporation into organic polymers.[13–15] These new materials have provided substantial enhancements in thermal stability,[16] mechanical[17] or electrical properties.[18] Recent advances have seen many new POSS species prepared by cross-metathesis,[19–21] hydrolysis of $RSiY_3$[22] or hydrosilylation.[23,24]

In our previous work, POSS based dendrimers bearing terminal -SiMe$\{((CH_2)_2)PPh_2\}_2$ groups have been obtained *via* successive hydrosilylation/alkenylation and shown significant positive dendritic effect on the regioselectivity of the hydroformylation of oct-1-ene.[25] As part of an ongoing project involving the synthesis of POSS based catalysts for asymmetric hydroformylation, we became interested in binding diazaphospholidine ligands to the surface of this rigid cage-like structure trying to stimulate new positive dendritic effects. Despite having synthesized a series of new precursors of phosphine ligands containing different functional groups, their attachment to the POSS core was not straightforward. We therefore sought general and practical methods that would form POSS based dendrimers with synthetically useful functional groups, easily prepared in multigram quantities and avoiding acidic[26] or basic conditions[27,28] which might disrupt the POSS core.

Results and discussion

Laine and co-workers reported the synthesis of brominated octaphenylsilsesquioxanes as nanoconstruction sites by iron-catalyzed bromination of octaphenylsilsesquioxanes.[29] Depending on the reaction stoichiometry, they obtained an average number of bromine atoms per cube distributed mainly in the para position relative to the silicon. We here report two other methods of synthesis of bromophenyl terminated octavinylsilsesquioxanes with an exact number of bromine atoms per cube. (Scheme 1)†

The first route is the cross-metathesis of *p*-bromostyrene with octavinylsilsesquioxane catalyzed by Grubbs' catalyst (1st generation) which occurred readily in CH_2Cl_2, as monitored by ^1H NMR spectroscopy. After total disappearance of the vinylsilyl signal (90 h), the compound was separated by precipitation in MeOH, followed by column chromatography affording **POSS-A** as a white powder in 90% yield. The second pathway lies in the hydrosilylation of OVS with either freshly prepared (3,5-dibromophenyl)dimethylsilane or (*p*-bromophenyl)dimethylsilane[31] catalyzed by Karstedt's catalyst (tetramethyldivinyldisiloxaneplatinum(0) in xylene) producing respectively **POSS-B** in 73% yield and **POSS-C** in 67% yield. The

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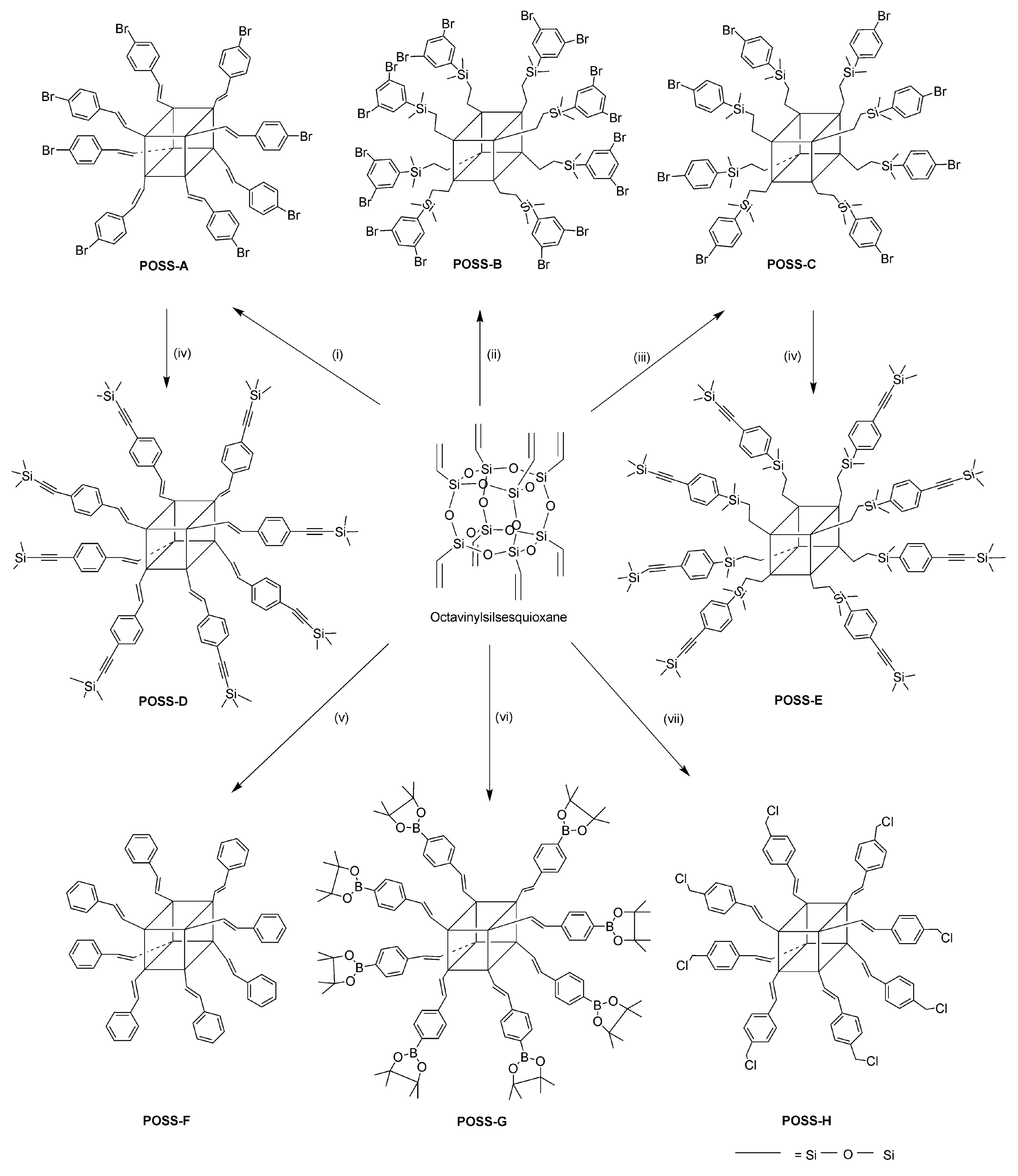
† During the time that this paper was with the reviewers, the Grubbs method for the synthesis of **A** and related molecules has been reported by another group.[30]



Scheme 1 The preparation and structures of a variety of different POSS based dendrimers suitable for further elaboration. Reagents and conditions: (i) 4-bromostyrene, Grubbs' catalyst (1st gen.), CH_2Cl_2; (ii) (3,5-dibromophenyl)dimethylsilane, Karstedt's catalyst, Et_2O; (iii) 4-bromophenyl(dimethyl)-silane, Karstedt's catalyst, Et_2O; (iv) trimethylsilylacetylene, $[Pd(PPh_3)_2Cl_2]$, CuI, PPh_3, Et_3N/THF; (v) iodobenzene, $[Pd(OAc)_2]$, PPh_3, Et_3N/THF; (vi) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene, Grubbs' catalyst (1st gen.), CH_2Cl_2; (vii) 4-vinybenzyl chloride, Grubbs' catalyst (1st gen.), CH_2Cl_2.

quite flexible **POSS-B**, as opposed to the more rigid starting cube of Laine,[29] displays 16 reactive groups at the generation 1, precisely distributed on each phenyl ring, thus offering the possibility of bearing numerous functional groups at very low generation. Other authors have reported the transformation of bromo functionality in POSS molecules *via* transition metal catalysed coupling into different chromophores, such as fluorenes[32] and oligophenylenes.[29,33,34] Under standard Sonogashira coupling conditions,[35] trimethylsilylacetylene groups were substituted onto the surface of **POSS-A** and **POSS-C** to give the corresponding *p*-trimethylsilylacetylene protected terminal alkynes, **POSS-D** and **POSS-E** in moderate yield after column chromatograpy. The deprotection of these latter by methanolic K_2CO_3 would produce interesting alkyne terminated dendrimers, the reactivity of which turns them into very attractive synthetic platforms on which to build new hybrid nanomaterials.

The palladium catalyzed reaction of iodobenzene with octavinylsilsesquioxane under standard Heck conditions[36] (5% $Pd(OAc)_2$, 10% PPh_3) in refluxing THF/Et_3N at 80 °C for 48 h afforded **POSS-F** in 51% yield (Scheme 1). X-ray quality crystals of **POSS-F** were obtained by recrystallisation from cold petroleum ether/CH_2Cl_2. The same molecule was also synthesized by Kubicki and coworkers using silylative coupling or cross-metathesis catalyzed by ruthenium complexes and identical X-ray data were obtained.[20] It has to be noticed that Sellinger *et al.*[37] in a similar Heck reaction between octavinysilsesquioxane and haloaromatic compounds obtained a mixture of 3–10 substituted compounds.

An alternative strategy for the use of octavinylsilsesquioxane as cubic building blocks was the Suzuki coupling reaction. Zhang and coworkers[33] reported that this coupling did not work well for the synthesis of their quantum dot-like organic-inorganic clusters whilst Laine and coworkers[38] reported that Suzuki coupling in a biphasic water/toluene solution using polybromophenylsilsesquioxanes with a variety of aryl borate dendrons gave very high conversions (> 99%). Conversely to Laine, we synthesized **POSS-G** with eight aryl borate groups, suitable for Suzuki coupling, on the surface of the cube by using p-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene as monomer,[36] prepared from styrene-4-boronic acid and pinacol in anhydrous diethyl ether (Scheme 1). Under cross-metathesis conditions and after the disappearance of the vinylsilyl signal (checked by ^1H NMR spectroscopy, 66 h) the mixture was filtered, concentrated, and treated with MeOH to effect precipitation. The by-product was first eluted from a silica gel column with CH_2Cl_2/petroleum ether (3:1), followed by **POSS-G** with CH_2Cl_2/ethyl acetate (4:1) affording a white powder in 51% yield. Finally, **POSS-H** decorated with benzyl chloride groups was obtained *via* Grubbs cross-metathesis in high yield under the same conditions described above. It may act as the starting material of new interesting compounds, as nucleophilic substitution of the chlorine atoms should be relatively easy.

Besides the total disappearance of the vinylsilyl signal of octavinylsilsesquioxane, another tool in checking the complete functionalisation of the new Grubbs compound and that the cube remains intact lies in $^{29}Si^1H$ HMQC 2D NMR as described in Fig. 1. The unique cross peak which appears on this 2D NMR spectrum of **POSS-H** corresponds to the clean coupling between a corner silicon atom and the nearest alkenyl proton. Unfortunately no correct microanalyses have been obtained for this compound as precipitation solvents are well trapped in the architecture of the cube, but the ^{29}Si NMR resonance at δ −78.9 ppm indicates that the cube is intact and unique and the cross peak shows that each corner is equivalent. ^1H NMR analysis of all the products showed that *E* double bonds were formed exclusively, resonances from protons attached to *Z* double bonds were below the detection limit.

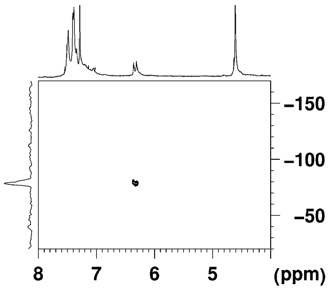


Fig. 1 $^{29}Si^1H$ HMQC 2D NMR spectrum of **POSS-H**.

All the compounds were characterized further by ^{13}C NMR, MALDI-TOF mass spectroscopy and microanalysis (see experimental section).

Experimental

All manipulations were carried out under dry, deoxygenated (Cr^{II} on silica) nitrogen using standard Schlenk techniques. Solvents THF, diethyl ether, (40–60 °C) light petroleum were distilled from sodium diphenyl ketyl; CH_2Cl_2 was treated with calcium hydride and degassed. Octavinylsilsesquioxane,[39] p-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene[36] and 4-bromophenyl(dimethyl)silane[31] were prepared using the literature methods. All starting materials were purchased from Aldrich. Melting points were carried out with Gallenkamp Melting Point Apparatus (uncorrected). Microanalyses were carried out by the University of St. Andrews Microanalysis service on a Carlo Erba 1110 CHNS analyzer. NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 NMR spectrometer. The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded with reference to tetramethylsilane. Matrix assisted laser desorption/ionization (MALDI) mass spectra were obtained using a Micromass TOF Spec 2E mass spectrometer system equipped with a 337 nm N_2 laser operating in the positive ion detection mode. Samples were generated by addition to the matrix (α-cyano-4-hydroxycinnamic acid or 2,5-dihydroxybenzoic acid, with NaI as an ionization promoter) and dissolved in a suitable solvent (THF or CH_2Cl_2) before being transferred to the sample holder and dried. The spectra were calibrated using a mixture of 4 peptides, angiotensin I & II, Renin substrate & ACTH clip (18–39).

Syntheses

(3,5-dibromophenyl)dimethylsilane. n-Butyllithium (25.4 cm^{-3}, 2.5 mol dm^{-3} in hexane, 63.5 mmol) was added to a cooled solution (−78 °C) of 1,3,5-tribromobenzene (20 g, 63.5 mmol) in diethylether (90 cm^{-3}) and stirred at this temperature for 1h. The resulting lithium reagent was transferred *via* canula to a solution of chlorodimethylsilane (7.1 cm^{-3}, 6.01 g, 63.5 mmol) in diethylether (30 cm^{-3}) over a period of 20 min. and stirred overnight at room temperature. After filtration, the solvent was evaporated and the residue distilled *in vacuo* (90–95 °C/0.3 mmHg) to give a colorless oil (16.6 g, 89%) (Found: C, 31.9; H 3.6. $C_8H_{10}SiBr_2$ requires C, 32.7; H, 3.4%); δ_H(400.13 MHz; $CDCl_3$; Me_4Si) 0.37 (6 H, d, *J* 3.8, $Si(CH_3)_2$), 4.30 (1 H, m, SiH), 7.57 (2 H, d, *J* 1.9) and 7.70

(1 H, t, *J* 1.9); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) −4.0 ($Si(CH_3)_2$), 123.3, 134.6, 135.2 and 142.9; δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) −15.7.

POSS-A. An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with octavinylsilsesquioxane (632 mg, 1 mmol) and 4-bromostyrene (2.3 g, 12 mmol) in CH_2Cl_2 (30 cm^{-3}). A solution of Grubbs' catalyst (33 mg, 0.04 mmol) in CH_2Cl_2 (3 cm^{-3}) was injected into the mixture heated at 55 °C. The reaction was stopped and cooled to room temperature after disappearance of the vinyl signals in the ^{1}H NMR spectrum (90 h.). The mixture was filtered and concentrated *in vacuo.* The compound was precipitated by addition of the concentrated solution of the crude product in CH_2Cl_2 to MeOH (300 cm^{-3}). The precipitation procedure was repeated twice and the residue subjected to silica gel column chromatography (petroleum ether/CH_2Cl_2 3:1), affording a white powder (1.68 g, 90%) (Found: C, 41.3; H, 2.3. $C_{64}H_{48}O_{12}Si_8Br_8$ requires C, 41.0; H, 2.6%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 6.24 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.29 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.34 (16 H, d, *J* 8.4) and 7.47 (16 H, d, *J* 8.4); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 118.3, 123.6, 128.8, 132.3, 136.4 and 148.5; *m/z* (MALDI) 1895.88 (M + Na. $C_{64}H_{48}O_{12}Si_8Br_8Na$ requires 1895.97).

POSS-B. Octavinylsilsesquioxane (1.36 g, 2.1 mmol) and freshly prepared (3,5-dibromophenyl)dimethylsilane (7.89 g, 26.9 mmol) were dissolved in diethylether (60 cm^{-3}) under nitrogen. Karstedt's catalyst (tetramethyldivinyldisiloxane)platinum(0) in xylene, 75 µl) was added to the solution at room temperature. The mixture became deep green after it was stirred for 30 min. It was then refluxed for 16 h. at 50 °C until the ^{1}H NMR spectrum showed that there was no double bond left. The mixture was cooled to room temperature, filtered and concentrated *in vacuo.* The excess (3,5-dibromophenyl)dimethylsilane was removed by Kugelröhr distillation. The residue was loaded onto a silica gel column and eluted with petroleum ether to afford a white solid (4.7 g, 73%) which was recrystallised from cold ethanol (Found: C, 32.3; H, 3.6. $C_{80}H_{104}Si_{16}Br_{16}O_{12}$ requires C, 32.2; H, 3.5%); δ_H(400.13 MHz; $CDCl_3$; Me_4Si) 0.26 (48 H, s, $Si(CH_3)_2$), 0.54 (16 H, m, $O_3SiCH_2CH_2Si$), 0.73 (16 H, m, $O_3SiCH_2CH_2Si$), 7.48 (16 H, d, *J* 1.7) and 7.68 (8 H, t, *J* 1.7); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) −3.7 ($Si(CH_3)_2$), 4.5 ($O_3SiCH_2CH_2Si$), 6.9 ($O_3SiCH_2CH_2Si$), 123.3, 134.4, 134.7 and 144.6; δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) −66.0 (O_3Si) and 1.4 ($Si(CH_3)_2$); *m/z* (MALDI) 3008.67 (M + Na. $C_{80}H_{104}Si_{16}Br_{16}O_{12}Na$ requires 3007.48).

POSS-C. Octavinylsilsesquioxane (518 mg, 0.8 mmol) and freshly prepared 4-bromophenyl(dimethyl)silane (2.15 g, 10 mmol) were dissolved in diethylether (60 cm^{-3}) under nitrogen. Karstedt's catalyst (tetramethyldivinyldisiloxane)platinum(0) in xylene, 75 µl) was added to the solution at room temperature. The mixture became deep green after it was stirred for 30 min. It was then refluxed for 16 h. at 50 °C until the ^{1}H NMR spectrum showed that there was no double bond left. The mixture was cooled to room temperature, filtered and concentrated *in vacuo.* The excess 4-bromophenyl(dimethyl)silane was removed by Kugelröhr distillation. The residue was dissolved in a minimum amount of THF and precipitated with methanol. The precipitate was collected, dried, loaded onto a silica gel column and eluted with petroleum ether to afford a white solid (1.3 g, 67%). A crystalline compound was obtained by recrystallisation from cold petroleum ether (Found: C, 40.8; H, 4.8. $C_{80}H_{112}Br_8O_{12}Si_{16}$ requires C, 40.2; H, 4.6%); mp 102 −104 °C (from petroleum ether); ν_{max}(KBr disk)/cm^{-1} 2953, 1573, 1251, 1107 and 1067; δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 0.00 (48 H, s, $Si(CH_3)_2$), 0.25 (16 H, m, $O_3SiCH_2CH_2Si$), 0.48 (16 H, m, $O_3SiCH_2CH_2Si$), 7.09 (16 H, d, *J* 8.5) and 7.24 (16 H, d, *J* 8.5); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) − 3.3 ($Si(CH_3)_2$), 4.8 ($O_3SiCH_2CH_2Si$), 7.4 ($O_3SiCH_2CH_2Si$), 124.2, 131.3, 135.5 and 138.1; *m/z* (MALDI) 2361.59 (M(Br^{79}). $C_{80}H_{112}Br_8O_{12}Si_{16}$ requires 2362.08).

POSS-D. In a Schlenk flask, **POSS-A** (500 mg, 0.27 mmol), [$Pd(PPh_3)_2Cl_2$] (150 mg, 0.21 mmol), CuI (82 mg, 0.43 mmol), PPh_3 (113 mg, 0.43 mmol) and Et_3N (8 cm^{-3}) were dissolved in THF (15 cm^{-3}) under argon. After vigorous stirring of the solution for 15 min. at 50 °C, trimethylsilylacetylene (1.5 cm^{-3}, 10.6 mmol) in THF (10 cm^{-3}) was slowly dropped into the mixture over 2 h. It was then stirred at 80 °C for 72 h under argon, cooled to room temperature and filtered to remove the insoluble salt. The solvent was evaporated *in vacuo* and the crude product purified by silica gel column (petroleum ether/CH_2Cl_2 3:1) affording a pale yellow powder (150 mg, 37%) (Found: C, 61.5; H, 6.3. $C_{104}H_{120}O_{12}Si_{16}$ requires C, 62.1; H, 6.0%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 0.26 (72 H, s, $Si(CH_3)_3$), 6.26 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.33 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.43 (16 H, d, *J* 8.4) and 7.46 (16 H, d, *J* 8.4); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 0.0 ($Si(CH_3)_3$), 104.9, 105.0, 118.2, 123.7, 126.8, 132.3, 137.1 and 148.5; *m/z* (MALDI) 2033.91 (M + Na. $C_{104}H_{120}O_{12}Si_{16}Na$ requires 2033.32).

POSS-E. In a Schlenk flask, **POSS-C** (228 mg, 0.096 mmol), [$Pd(PPh_3)_2Cl_2$] (75 mg, 0.11 mmol), CuI (41 mg, 0.22 mmol), PPh_3 (56 mg, 0.21 mmol) and Et_3N (5 cm^{-3}) were dissolved in THF (10 cm^{-3}) under argon. After vigorous stirring of the solution for 15 min. at 50°C, trimethylsilylacetylene (0.75 cm^{-3}, 5.3 mmol) in THF (5 cm^{-3}) was slowly dropped into the mixture over 1 h. It was then stirred at 80 °C for 72 h under argon, cooled to room temperature and filtered to remove the insoluble salt. The solvent was evaporated *in vacuo* and the crude product purified by silica gel column (petroleum ether/CH_2Cl_2 4:1) affording a white powder (150 mg, 47%) (Found: C, 58.2; H, 7.4. $C_{120}H_{184}O_{12}Si_{24}$ requires C, 57.8; H, 7.4%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 0.00 (48 H, s, $Si(CH_3)_2$), 0.03 (72 H, s, $Si(CH_3)_3$), 0.24 (16H, m, $O_3SiCH_2CH_2Si$), 0.46 (16 H, m, $O_3SiCH_2CH_2Si$) and 7.18 (32 H, m); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) −3.7 $Si(CH_3)_2$, 0.0 ($Si(CH_3)_3$), 4.4 ($O_3SiCH_2CH_2Si$), 7.0 ($O_3SiCH_2CH_2Si$), 94.7, 105.2, 123.5, 131.0, 133.4 and 139.9; *m/z* (MALDI) 2516.22 (M + Na. $C_{120}H_{184}O_{12}Si_{24}Na$ requires 2514.12).

POSS-F. A Schlenk flask was charged under argon with octavinylsilsesquioxane (316 mg, 0.5 mmol), [$Pd(OAc)_2$] (45 mg, 0.2 mmol) and PPh_3 (105 mg, 0.4 mmol) in THF/Et_3N (14 cm^{-3}/4 cm^{-3}). The resulting mixture was stirred for 15 min. and iodobenzene (1.22 g, 6 mmol) was added. It was then heated at 80 °C for 48 h. After cooling to room temperature, the mixture was filtered and concentrated *in vacuo.* The residue was dissolved in a small amount of CH_2Cl_2 and precipitated in methanol. The procedure was repeated once more and the crude product collected, dried, loaded onto a silica gel column and eluted with CH_2Cl_2 to afford a white solid. A crystalline compound was obtained by recrystallisation from cold petroleum ether/CH_2Cl_2 (316 mg, 51%) (Found: C, 61.46; H, 4.14. $C_{64}H_{56}O_{12}Si_8$ requires

C, 61.90; H, 4.54%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 6.35 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.33 (24 H, m), 7.41 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$) and 7.50 (16 H, m); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 117.8, 127.4, 129.0, 129.3, 137.7 and 149.6; *m/z* (MALDI) 1264.70 (M + Na. $C_{64}H_{56}O_{12}Si_8Na$ requires 1263.28).

POSS-G. An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with octavinylsilsesquioxane (316 mg, 0.5 mmol) and p-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene (1.8 g, 8 mmol) in CH_2Cl_2 (20 cm^{-3}). A solution of Grubbs' catalyst (26 mg, 0.03 mmol) in CH_2Cl_2 (2 cm^{-3}) was injected in the mixture heated at 55 °C. The reaction was stopped and cooled to room temperature after disappearance of the vinyl signals in the ^{1}H NMR spectrum (66 h.). The mixture was filtered and the solution concentrated. The crude compound was precipitated by adding the concentrated solution to MeOH (300 cm^{-3}) and subjected to silica gel column. The first fraction was removed by CH_2Cl_2/petroleum ether (3:1) as eluent whilst the desired product was eluted with CH_2Cl_2/ethyl acetate (4:1) affording a white powder (573 mg, 51%) (Found: C, 59.5; H, 6.7. $C_{112}H_{144}O_{28}B_8Si_8$ requires C, 59.8; H, 6.5%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 1.27 (96 H, s, CH_3), 6.26 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.33 (8 H, d, *J* 19.2, $O_3SiCH{=}CH$), 7.41 (16 H, d, *J* 8.2) and 7.69 (16 H, d, *J* 8.2); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 25.3 (CH_3), 118.9, 126.6, 135.5, 140.2 and 149.6; δ_{Si}(79.5 MHz; C_6D_6; Me_4Si) −78.37 (O_3Si); *m/z* (MALDI) 2272.6 (M + Na. $C_{112}H_{144}O_{28}B_8Si_8Na$ requires 2272.4).

POSS-H. An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with octavinylsilsesquioxane (200 mg, 0.32 mmol) and 4-vinybenzyl chloride (834 mg, 5.5 mmol) in CH_2Cl_2 (8 cm^{-3}). A solution of Grubbs' catalyst (10 mg, 0.01 mmol) in CH_2Cl_2 (1 cm^{-3}) was injected in the reaction mixture at 55 °C. The reaction was stopped and cooled to room temperature after disappearance of the vinyl signals in the ^{1}H NMR spectrum (90 h.). The mixture was filtered and the solution concentrated. The compound was precipitated by addition of the concentrated solution of the crude product in CH_2Cl_2 to EtOAc/petroleum ether (10 cm^{-3}/50 cm^{-3}). The precipitation procedure was repeated twice affording a white powder (333 mg, 65%). δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 4.61 (16 H, s, CH_2), 6.33 (8 H, d, *J* 18.9, $O_3SiCH{=}CH$), 7.42 (8H, d, *J* 18.9, $O_3SiCH{=}CH$, confirmed by ^{1}H - ^{1}H COSY) and 7.46 (32 H, m); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 45.9 (CH_2), 118.2, 127.1, 128.6, 137.6, 137.7, and 148.2; δ_{Si}(79.5 MHz; C_6D_6; Me_4Si) −78.9 (O_3Si); *m/z* (MALDI) 1595.3 (M-(Cl^{35}). $C_{72}H_{64}O_{12}Cl_7Si_8$ requires 1593.9).

Conclusions

In conclusion, the eight terminal vinyl groups around octavinylsilsesquioxane have been successfully functionalized by Heck coupling, cross-metathesis (Grubbs' catalyst), hydrosilylation (Karstedt's catalyst) and Sonogashira coupling. A variety of new functionalisable dendrimer cores based on octavinylsilsesquioxane have been synthesized and characterized by NMR spectroscopy, MALDI-TOF mass spectroscopy and microanalysis. Further work on synthesis of inorganic-organic functionalized materials using these cores will be reported elsewhere.

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Notes and references

1 D. A. Tomalia, A. M. Naylor and W. A. Goddard III, *Angew. Chem. Int. Ed.*, 1990, **29**, 138.

2 C. J. Hawker and J. M. J. Fréchet, *J. Chem. Soc. Chem. Commun.*, 1990, 1010.

3 A. Momotake and T. Arai, *Polymer*, 2004, **45**, 5369.

4 U. Boas, J. B. Christensen, and P. M. H. Heegard, *Dendrimers in Medicine and Biotechnology: New Molecular Tools*, Royal Society of Chemistry edn., Cambridge, UK, 2006.

5 L. H. Gade, *Dendrimer Catalysis*, Springer GmbH edn., Berlin, Germany, 2006.

6 B. Helms and J. M. J. Fréchet, *Adv. Synth. Catal.*, 2006, **348**, 1125.

7 P. L. Burn, S.-C. Lo and I. D. W. Samuel, *Adv. Mater.*, 2007, **19**, 1675.

8 S.-C. Lo and P. L. Burn, *Chem. Rev.*, 2007, **107**, 1097.

9 J. Dobler, M. Pritzsche and J. Sauer, *J. Am. Chem. Soc.*, 2005, **127**, 10861.

10 A. R. Bassindale, D. J. Parker, M. Pourny, P. G. Taylor, P. N. Horton and M. B. Hursthouse, *Organometallics*, 2004, **23**, 4400.

11 J. Choi, J. Harcup, A. F. Yee, Q. Zhu and R. M. Laine, *J. Am. Chem. Soc.*, 2001, **123**, 11420.

12 R. M. Laine, *J. Mater. Chem.*, 2005, **15**, 3725.

13 J. Choi, S. G. Kim and R. M. Laine, *Macromolecules*, 2004, **37**, 99.

14 K. Liang, G. Li, H. Toghiani, J. H. Koo and C. U. Pittman, *Chem. Mater.*, 2006, **18**, 301.

15 L. Zheng, S. Hong, G. Cardoen, E. Burgaz, S. P. Gido and E. B. Coughlin, *Macromolecules*, 2004, **37**, 8606.

16 H. Y. Xu, S. W. Kuo, J. Y. Lee and F. C. Chang, *Polymer*, 2002, **43**, 5117.

17 S. A. Pellice, D. P. Fasce and R. J. J. Williams, *J. Polym. Sci. Part B: Polym. Phys.*, 2003, **41**, 1451.

18 K. Su, D. R. Bujalski, K. Eguchi, G. V. Gordon, S. Hu and D.-L. Ou, *J. Mater. Chem.*, 2005, **15**, 4115.

19 F. J. Feher, D. Soulivong, A. G. Eklund and K. D. Wyndham, *Chem. Commun.*, 1997, 1185.

20 Y. Itami, B. Marciniec and M. Kubicki, *Chem. Eur. J.*, 2004, **10**, 1239.

21 S.-C. Lo, C. Zhen, M. Lauters, G. E. Jabbour and A. Sellinger, *J. Am. Chem. Soc.*, 2007, **129**, 5808.

22 A. R. Bassindale, Z. Liu, I. A. MacKinnon, P. G. Taylor, Y. Yang, M. E. Light, P. N. Horton and M. B. Hursthouse, *Dalton Trans.*, 2003, 2945.

23 J. D. Froehlich, R. Young, T. Nakamura, Y. Ohmori, S. Li and A. Mochizuki, *Chem. Mater.*, 2007, **19**, 4991.

24 K. Wada, N. Watanabe, K. Yamada, T. Kondo and T.-A. Mitsudo, *Chem. Commun.*, 2005, 95.

25 L. Ropartz, R. E. Morris, D. F. Foster and D. J. Cole-Hamilton, *Chem. Commun.*, 2001, 361.

26 F. J. Feher, D. Soulivong and A. G. Eklund, *Chem. Commun.*, 1998, 399.

27 F. J. Feher, R. Terroba and J. W. Ziller, *Chem. Commun.*, 1999, 2153.

28 E. Rikowski and H. C. Marsmann, *Polyhedron*, 1997, **16**, 3357.

29 C. M. Brick, R. Tamaki, S.-G. Kim, M. Z. Asuncion, M. Roll, T. Nemoto, Y. Ouchi, Y. Chujo and R. M. Laine, *Macromolecules*, 2005, **38**, 4655.

30 S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson, III and R. M. Laine, *Chem. Mater.*, 2008, DOI: 10.1021/cm801017e.

31 M. Ishikawa, K. Watanabe, H. Sakamoto and A. Kunai, *J. Organomet. Chem.*, 1993, **455**, 61.

32 J. Lee, H.-J. Cho, B.-J. Jung, N. S. Cho and H.-K. Shim, *Macromolecules*, 2004, **37**, 8523.
33 C. He, Y. Xiao, J. Huang, T. Lin, K. Y. Mya and X. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 7792.
34 Y. Xiao, L. Liu, C. He, W. S. Chin, T. Lin, K. Y. Mya, J. Huang and X. Lu, *J. Mater. Chem.*, 2005, **16**, 829.
35 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467.
36 M. Nicolas, B. Fabre, G. Marchand and J. Simonet, *Eur. J. Org. Chem.*, 2000, 1703.
37 A. Sellinger, R. Tamaki, R. M. Laine, K. Ueno, H. Tanabe, E. Williams and G. E. Jabbour, *Chem. Commun.*, 2005, 3700.
38 C. M. Brick, Y. Ouchi, Y. Chujo and R. M. Laine, *Macromolecules*, 2005, **38**, 4661.
39 M. Voronkov, T. N. Martynova, R. G. Mirskov and V. I. Bely, *J. Gen. Chem. USSR (Engl. Transl.)*, 1979, **49**, 1328.