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Synthesis of aldehyde functionalised polyhedral oligomeric silsesquioxanes

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Hydrosilylation reactions have been used to functionalise the exterior surfaces of octavinyloctasilsesquioxane molecules to provide routes to octaaldehyde molecules. These have been characterised by NMR and MALDI (matrix assisted laser desorption/ionisation)-TOF mass spectroscopy. Further reactions of the molecules to produce carboxylic acid and Schiff base functionalised species are also reported. The effect of temperature and catalyst on the regioselectivity of the reaction is discussed.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS, $R_8Si_8O_{12}$) provide an excellent platform for the synthesis of new inorganic–organic hybrid materials.[1,2] Their well defined, almost cubic silica-like core surrounded by eight organic groups makes them topologically ideal for the preparation of intimate nanocomposite materials,[3] with the size of the inorganic region precisely defined by the size of the core. This has led to proposed uses of these molecules as hard blocks or reinforcing particles in high performance polymer materials.[4] These polymers show many improved properties over those that use more traditional fillers (such as silica), including higher use temperatures and increased fire retardance. The cubic topology of the molecule also leads to some interesting opportunities to prepare micro- or mesoporous materials, as it is geometrically difficult to link cubes through only their corners and still fill all available space, although the degree of porosity must depend on the efficiency of polymerisation and the flexibility of the organic polymerisable group.[5–7]

The shape of the silica core of the molecule also lends itself well to the preparation of dendritic materials, where the large number of external branching sites on the core leads to a high concentration of dendrimer branch ends after relatively few generations.[8–11] These types of dendrimers have been studied as potential catalysts, and when functionalised on the exterior with ligands such as phosphines some very interesting effects have been observed, including the first report of a positive dendrimer effect on the selectivity of reactions.[12,13]

The fact that the length scales and interfacial interactions between inorganic and organic regions of the structures are precisely defined, unlike many composite materials, provides an opportunity to study the fundamental affects of systematically altering the various regions of the structure. In this way, structure–property relationships can be built up that will help define the strategies to be used in the design of future nanocomposite materials. In order to achieve this goal, which is equally applicable in both polymer and dendrimer studies, suitable POSS monomers must be available. Recent advances have seen many new POSS species prepared.[14] Hydrosilylation, addition of Si–H to an olefinic double bond, has been an especially useful synthetic methodology, leading to various types of dendrimer and 'octopus' molecules.[3,15] In this paper we present the synthesis of octaaldehyde POSS species. The reactivity of the aldehyde functional group makes it an attractive synthetic platform on which to build new ligands for inorganic and organic derivatives of POSS molecules, new dendrimers and new monomers for copolymerisation.

Experimental

All manipulations were carried out under an atmosphere of argon. 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. FTIR spectra were recorded on a Perkin-Elmer 1710 spectrometer. Chemical analysis was accomplished by the University of St. Andrews Microanalysis service on a Carlo Erba model 1106 elemental analyser.

Synthesis

The starting materials for these preparations, octavinylpentacyclooctasiloxane (octavinyloctasilsesquioxane, **1**), 2-(4-bromophenyl)-1,3-dioxolane and 2-(3-bromophenyl)-1,3-dioxolane, were prepared using the literature methods.[16,17]

2-(4-(Dimethylsilyl)phenyl)-1,3-dioxolane 2. 62 mmol of 4-(1,3-dioxolan-2-yl)phenylmagnesium bromide in 110 ml of THF (prepared from 1.53 g of Mg and 14.18 g of 2-(4-bromophenyl)-1,3-dioxolane) were added to 5.86 g (62 mmol) of chlorodimethylsilane in THF (20 ml). The solution was stirred at room temperature overnight. Sodium hydrogen carbonate (1 M in water, 80 ml) was added and solution extracted with diethyl ether (3 × 50 ml). The combined organic layers were washed with brine (60 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The residue (11.42 g) was purified by distillation under reduced pressure yielding 9.35 g (73%) of compound **2** as a colourless oil. bp 82 °C (0.2 mmHg) (Found: C, 63.15; H, 8.16. $C_{11}H_{16}O_2Si$ requires C, 63.42; H, 7.74%). ^{1}H NMR ($CDCl_3$): δ 0.38 (6 H, d, J = 3.8, $SiCH_3$), 4.15 (4 H, m, OCH_2CH_2O), 4.47 (1 H, sept, J = 3.8, SiH), 5.86 (1 H, s, OCHO), 7.51 (2 H, d, J = 8.0, CH) and 7.61 (2 H, d, J = 8.0 Hz, CH). ^{13}C NMR ($CDCl_3$): δ −3.7 ($SiCH_3$), 65.3 (2 C, OCH_2-CH_2O), 103.7 (OCHO), 125.8 (CH), 134.1 (CH), 138.7 and 138.9 (2 C, CSi and *C*CH). FTIR (NaCl, cm^{-1}): 3073 m, 3021

m, 2959 s, 2886 s, 2118 vs (Si-H), 1411 s, 1388 s, 1309 m, 1250 s, 1221 s, 1184 m, 1082 s, 1022 m, 970 m, 944 m, 881 s, 817 s, 767 s, 706 m and 627 m.

2-(3-(Dimethylsilyl)phenyl)-1,3-dioxolane 3. 65 mmol of 3-(1,3-dioxolan-2-yl)phenylmagnesium bromide in 120 ml of THF (prepared from 1.63 g of Mg and 15 g of 2-(3-bromophenyl)-1,3-dioxolane) were added to 6.17 g (65 mmol) of chlorodimethylsilane in THF (25 ml). Reaction as above gave rise to a residue (12.44 g) which was purified by distillation under reduced pressure yielding 10.5 g (78%) of **3** as a colourless oil. bp 83 °C (0.3 mmHg) (Found: C, 63.13; H, 8.14. $C_{11}H_{16}O_2Si$ requires C, 63.42; H, 8.14%). ^{1}H NMR ($CDCl_3$): δ 0.38 (6 H, d, J = 3.7, $SiCH_3$), 4.16 (4 H, m, OCH_2CH_2O), 4.47 (1 H, sept, J = 3.7 Hz, SiH), 5.85 (1 H, s, OCHO), 7.41 (1 H, m, CH), 7.54 (1 H, m, CH), 7.58 (1 H, m, CH) and 7.68 (1 H, s, CH). ^{13}C NMR ($CDCl_3$): δ −3.7 ($SiCH_3$), 65.4 (2C, OCH_2-CH_2O), 103.9 (OCHO), 127.3 (CH), 127.9 (CH), 132.0 (CH), 135.0, (CH), 137.1 and 137.7 (2C, CSi and *C*CH). FTIR (NaCl, cm^{-1}): 2969 s, 2887 s, 2119 vs (Si-H), 1475 m, 1423 s, 1368 s, 1251 s, 1222 s, 1121 s, 1093 vs, 1030 m, 888 s, 837 m, 797 m, 764 m, 735 m and 652 m.

1,3,5,7,9,11,13,15-Octakis{2-[4-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 4. 2-(4-(Dimethylsilyl)phenyl)-1,3-dioxolane **2** (3.41 g, 16 mmol) and platinum tetramethyldivinyldisiloxane (2.1–2.4% platinum in xylene, 10 drops) were added to a solution of octavinylpentacyclooctasiloxane **1** (1.0 g, 1.58 mmol) in diethyl ether (50 ml). The solution was stirred at room temperature for 20 min while an exotherm was observed, then refluxed for 10 h. The crude green solution was filtered on a 15 cm pad of silica gel (diethyl ether as eluent). The filtrate was concentrated *in vacuo* to give a colourless oil. The excess of 2-(4-(dimethylsilyl)phenyl)-1,3-dioxolane was removed by Kugelrohr distillation to yield compound **4** (2.88 g, 79%) as a colourless viscous oil (Found: C, 54.2; H, 6.7%). ^{1}H NMR ($CDCl_3$): δ 0.27 (48 H, s, $SiCH_3$), 0.54 (16 H, m, CH_2), 0.78 (16 H, m, CH_2), 4.11 (32 H, m, OCH_2-CH_2O), 5.85 (8 H, s, OCHO), 7.47 (16 H, d, J = 8.0, CH) and 7.53 (16 H, d, J = 8.0 Hz, CH). ^{13}C NMR ($CDCl_3$): δ −3.5 ($SiCH_3$), 4.5 (CH_2), 7.0 (CH_2), 65.3 (2C, OCH_2CH_2O), 103.7 (OCHO), 125.7 (CH), 133.7 (CH), 138.5 and 140.4 (2C, CSi and *C*CH). FTIR ($CDCl_3$, cm^{-1}): 2957 m, 2890 m, 1408 m, 1251 m, 1116 vs, 1022 m, 971 m, 944 m, 839 m and 815 m.

1,3,5,7,9,11,13,15-Octakis{2-[3-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 5. 2-(3-(Dimethylsilyl)phenyl)-1,3-dioxolane (1.97 g, 9.48 mmol) and platinum tetramethyldivinyldisiloxane (2.1–2.4% platinum in xylene, 6 drops) were added to a solution of octavinylpentacyclooctasiloxane **1** (0.5 g, 0.79 mmol) in diethyl ether (25 ml). The solution was stirred at room temperature for 10 min then treated as for compound **4**. The excess of 2-(3-(dimethylsilyl)-phenyl)-1,3-dioxolane was removed by a Kugelrohr distillation to yield **5** (1.18 g, 65%) as a colourless viscous oil (Found: C, 54.89; H, 6.99. $C_{26}H_{38}O_7Si_4$ requires C, 54.32 ; H, 6.66%). ^{1}H NMR ($CDCl_3$): δ 0.28 (48 H, s, $SiCH_3$), 0.30 (16 H, m, CH_2), 0.61 (16 H, m, CH_2), 4.09 (32 H, m, OCH_2CH_2O), 5.83 (8 H, s, OCHO), 7.38 (8 H, m, CH), 7.50 (16 H, m, CH) and 7.62 (8 H, s, CH). ^{13}C NMR ($CDCl_3$): δ −3.5 ($SiCH_3$), 4.5 (CH_2), 7.1 (CH_2), 65.3 (2C, OCH_2CH_2O), 104.0 (OCHO), 126.9 (CH), 127.8 (CH), 131.7 (CH), 134.6 (CH), 136.9 and 139.4 (2s, CSi and *C*CH). FTIR ($CDCl_3$, cm^{-1}): 2957 m, 2890 m, 1408 m, 1251 m, 1116 vs, 1022 m, 971 m, 944 m, 839 m and 815 m.

1,3,5,7,9,11,13,15-Octakis{2-[4-formylphenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 6. Pyridinium *p*-toluenesulfonate (0.6 g, 2.38 mmol), compound **4** (2.80 g, 1.21 mmol), and acetone (50 ml) were refluxed overnight. The solvent was removed *in vacuo* to afford 2.2 g of a very viscous oil which was crystallised from ethanol (10 ml) to give **6** as white crystals. mp 112 °C (Found: C, 53.32; H, 6.31. $C_{22}H_{30}$-O_5Si_4 requires C, 54.28; H, 6.21%). ^{1}H NMR ($CDCl_3$): δ 0.28 (48 H, s, $SiCH_3$), 0.52 (16 H, m, CH_2), 0.78 (16 H, m, CH_2), 7.62 (16 H, d, J = 7.8, CH), 7.80 (16 H, d, J = 7.8 Hz, CH) and 10.02 (8 H, s, CHO). ^{13}C NMR ($CDCl_3$): δ −3.7 ($SiCH_3$), 4.4 (CH_2), 6.9 (CH_2), 128.6 (CH), 133.6 (CSi), 134.0 (CH), 136.6 (*C*CHO) and 192.4 (CHO). FTIR (KBr disk, cm^{-1}): 2955 m, 2892 m, 1704 s, 1597 m, 1558 m, 1407 m, 1383 m, 1251 m, 1213 m, 1103 vs, 837 m, 812 m, 759 m, 692 m, 635 m and 551 m.

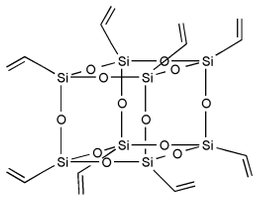
1,3,5,7,9,11,13,15-Octakis{2-[3-formylphenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 7. Pyridinium *p*-toluenesulfonate (0.480 g, 1.90 mmol), compound **5** (2.240 g, 0.97 mmol) and wet acetone (40 ml) were refluxed overnight. The solvent was removed under reduced pressure and diethyl ether (40 ml) used to re-dissolve the residue. This solution was washed with sodium hydrogencarbonate solution (1 M in water, 3 × 40 ml) followed by brine (40 ml) and the organic component then dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give a viscous, colourless oil (1.737 g, 92%) (Found: C, 54.75; H, 6.49%). ^{1}H NMR ($CDCl_3$): δ 0.28 (48 H, s, $SiCH_3$), 0.53 (16 H, m, CH_2), 0.78 (16 H, m, CH_2), 7.48 (8 H, m, CH), 7.71 (8 H, m, CH) 7.85 (8 H, m, CH), 7.99 (8H, s, CH) and 10.01 (8 H, s, CHO). ^{13}C NMR ($CDCl_3$): δ −3.6 ($SiCH_3$), 4.3 (CH_2), 7.0 (CH_2), 128.4, 130.6, 134.6, 135.6, 139.5, 140.4 (aromatic) and 192.7 (CHO). FTIR (NaCl, cm^{-1}): 2951 m, 2888 m, 1696 s, 1586 m, 1407 m, 1370 m, 1249 m, 1206 m, 1101 vs, 896 m, 870 m, 836 m, 754 m, 692 m, 650 m and 545 m.

1,3,5,7,9,11,13,15-Octakis{2-[4-(4-bromo-3,5-bis(dimethylaminomethyl)phenyliminomethyl)phenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 8. Pyridinium tosylate (100 mg) was refluxed with a solution of compound **4** (2.27 g, 1.37 mmol) in 10% aqueous acetone under argon overnight. Work-up of a small sample of the mixture showed complete deprotection to the aldehyde according to ^{1}H NMR. Toluene (100 cm^3) and 4-bromo-3,5-bis[(dimethylamino)methyl]aniline (prepared by the method of van de Kuil *et al.*[18]) (400 mg, 1.4 mmol) were added and the mixture refluxed under a Dean Stark condenser for 2 h. The products were washed with brine then dried over $MgSO_4$ and the solvent removed by evaporation to yield a very viscous brown oil (1.93 g, 74%). The residual aniline present was almost completely removed by washing with hexane and decanting off the solution from the oil. ^{1}H NMR ($CDCl_3$): δ 0.27 (48 H, s, $SiCH_3$), 0.54 (16 H, m, CH_2), 0.27 (16 H, m, CH_2), 2.30 (96 H, s, NCH_3), 3.58 (32 H, s, NCH_2), 7.20 (16 H, s, CH), 7.59 (16 H, d, J = 7.8, CH), 7.82 (16 H, d, J = 7.8 Hz, CH) and 8.42 (8 H, s, N=CH). ^{13}C NMR ($CDCl_3$): δ −3.8 ($SiCH_3$), 4.2 (CH_2), 6.8 (CH_2), 45.5 (NCH_3), 63.7 (NCH_2), 121.7 (CH), 123.6 (CBr), 127.8 (CH), 133.9 (CH), 136.4 (*C*CHN), 139.4 (*C*CH_2N), 143.6 (CSi), 150.6 (*C*N=CH) and 160.5 (HC=N); two small unidentified peaks are also present at 128.52 and 133.54.

Matrix assisted laser desorption/ionisation (MALDI) mass measurements were performed on a Micromass Tof Spec 2E mass spectrometer system (Manchester, UK) equipped with a 337 nm N_2 laser and operating in positive ion reflectron mode. Samples were dissolved in 1 : 1 ethanol–acetonitrile then prepared as an alpha matrix (α-cyano-4-hydroxycinnamic acid). All mass measurements stated refer to observed peaks for the most common isotopes (^{12}C, ^{1}H, ^{28}Si and ^{16}O) and so are not necessarily the most abundant species.

Results and discussion

In order to accomplish our goal of preparing functionalised POSS species using hydrosilylation, it is first necessary to identify suitable silane monomers containing the correct Si–H



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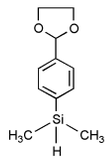

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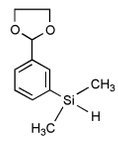

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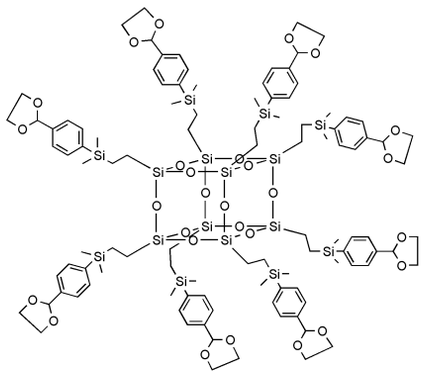

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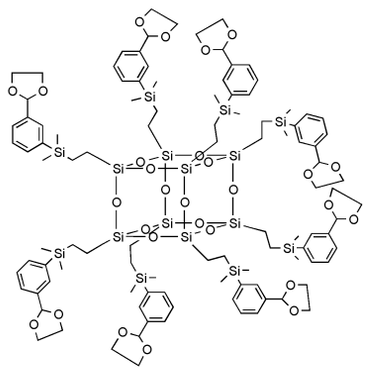

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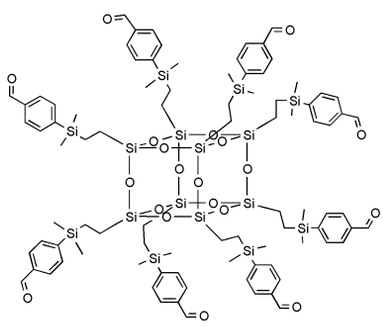

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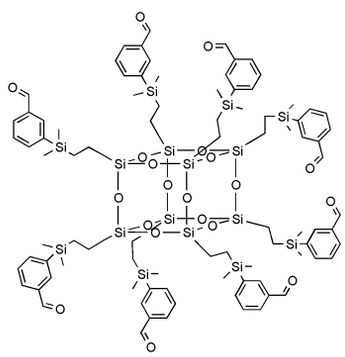

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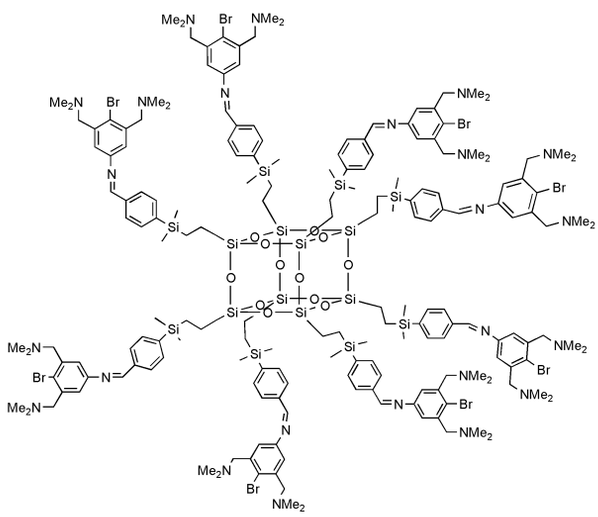

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functionality. The synthesis of **2** and **3** was accomplished using standard organic methodologies using a Grignard reagent prepared from the protected 3- or 4-bromobenzaldehyde, followed by addition of $HSi(CH_3)_2Cl$. Platinum catalysed hydrosilylation of octavinylpentacyclooctasiloxane **1** using protected aldehyde silanes **2** and **3** produced the functionalised POSS species **4** and **5**, with the dioxolane functionality in the 3 and 4 positions on the aromatic ring respectively. Protection of the aldehyde functional group is required during synthesis of the silane to prevent unwanted reaction, and is retained during the hydrosilylation to prevent any O-silylation at the oxygen. Nuclear magnetic resonance (^1H and ^{13}C) spectroscopy revealed that all the vinyl

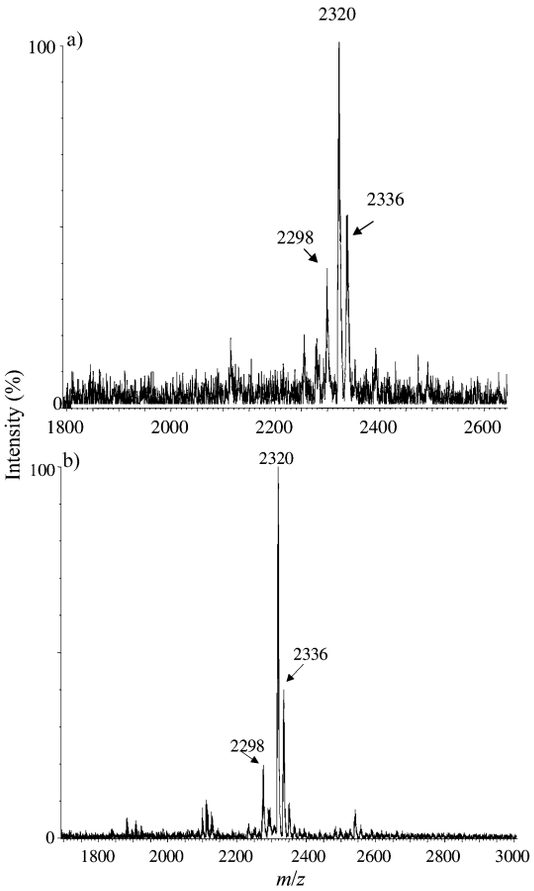

Fig. 1 MALDI-TOF mass spectra of dioxolanes **4** (a) and **5** (b). In both cases the *m*/*z* values of 2298, 2320 and 2336 can be attributed to the $[M + H]^+$, $[M + Na]^+$ and $[M + K]^+$ species respectively.

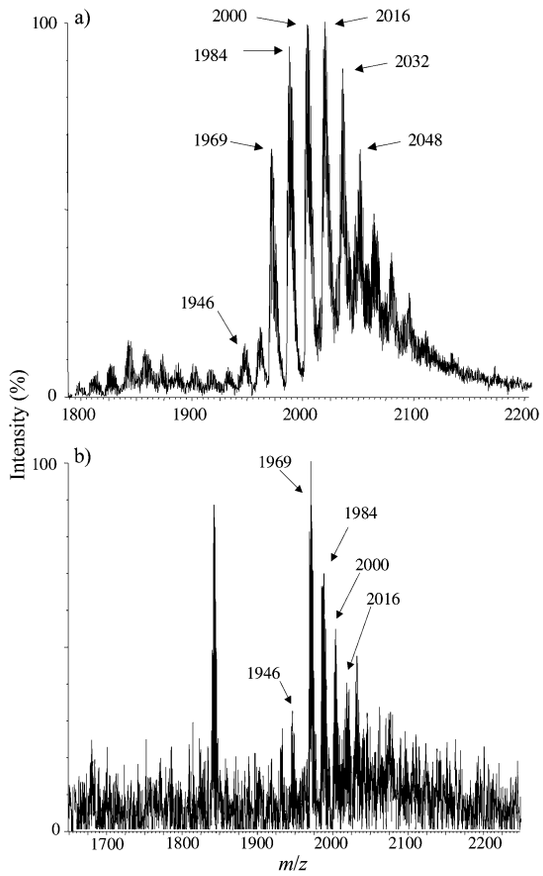

Fig. 2 MALDI-TOF mass spectra of aldehydes **6** (a) and **7** (b) after partial oxidation to carboxylic acids has occurred. In both cases a series of peaks with maxima differing by 16 *m*/*z* units can clearly be seen, indicating the additional mass of one oxygen atom per arm of the aldehyde up to a maximum of eight. In both cases the peak at *m*/*z* 1969 can be attributed to the octaaldehyde species + Na^+.

resonances on the cube had disappeared, indicating that, at least within the limits of detection by NMR, that the reaction had gone to completion. MALDI-TOF mass spectrometry (Fig. 1) and chemical analysis also indicated that the products were of the correct mass for addition to all the corners of the POSS cube, although in the case of the dioxolane in the 3 position an unidentified peak of lower mass is also present; recently Murfee *et al.* have reported MALDI/TOF spectra of POSS species where unusual fragmentation of the molecular ion has occurred, and such processes cannot be ruled out here.[19] A close look at the proton NMR spectrum revealed more complicated resonances in the methylene region than would have been expected for the structure as drawn. This can be accounted for by a small amount of addition at the β position, rather than at the α position (terminal CH_2) of the POSS vinyl groups. Many reports of hydrosilylation under similar conditions reveal that the reaction is often regioselective at the α position, especially when sterically hindered alkenes are used. However, in certain cases, such as the hydrosilylation of vinylsiloxanes to octahydridopentacyclosiloxanes (octahydrido-POSS) carried out by Bassindale and Gentle,[15] there was up to 30% β addition depending on the catalyst used. In our system, the problem of β addition is at worst 5%, and can be reduced markedly by careful control over the temperature. High temperatures, such as those used by Bassindale and Gentle (80 °C), seem to favour β addition, while lower temperatures (room temperature or reflux in diethyl ether) suppress this unwanted side reaction. Initial mixing of the reactions at ice bath temperatures may suppress it even further to the extent that the β addition has been reduced to levels that are difficult to quantify by NMR. Deprotection of the acetals **4** and **5** yields the aldehydes **6** and **7**.

The utility of the aldehyde-functionalised molecules is in the relatively wide range of facile derivatisation reactions that is possible. Two of the most obvious, and potentially most useful, are oxidation to carboxylic acids and Schiff-base condensation to imines. Both the 3- and 4- substituted octabenzaldehyde species convert over time when left exposed to air, compound **7** being slightly more susceptible to oxidation than **6**, although it is somewhat less clean, leading to a small amount of unidentified by-products. Analysis by MALDI-TOF mass spectroscopy (Fig. 2) at various stages of oxidation illustrates how species are formed containing *n* carboxylic groups, where *n* ranges from 0 for the freshly prepared octaaldehydes to 8 for fully oxidised species. The synthesis of octacarboxylic acid functionalised POSS species is attractive because of their potential uses in supramolecular chemistry and as building blocks in crystal engineering experiments. However, we have yet to prepare a pure sample of the octacarboxylic acid; unchanged aldehyde groups always contaminate it to some extent. About 4% of endgroups are still aldehyde after two months (as characterised by ^1H NMR and confirmed by CHN analysis). Attempts to use mild oxidising agents in solution have proved difficult because of solubility problems.

The reaction of octaaldehyde **6** with an amine to produce a molecule **8** is also an attractive proposition because of the resulting dendrimer's resemblance to those that have previously been used as catalysts. Proton NMR experiments indicated that the reaction had gone to completion after a relatively short time. However, as is often the case in the preparation of larger dendrimer species such as this, removal of contaminating solvent and unchanged starting material, especially the 4-bromo-3,5-bis[(dimethylamino)methyl]aniline is difficult, presumably because they become trapped between the arms of the molecule.

Conclusion

This work reports the synthesis and full characterisation of dioxolane and aldehyde functionalised dendrimers. The new molecules have been characterised by NMR, microanalysis and MALDI-TOF mass spectroscopy. The conditions of synthesis are shown to be important in determining whether the initial hydrosilylation reaction occurs at the α or β positions. Reaction of the dendrimers to form carboxylic acid and Schiff base species and their preliminary characterisation by NMR and MALDI-TOF mass spectroscopy is also reported. Further investigations of these molecular species are currently in progress to determine their suitability for use in the preparation of polymeric materials and dendrimer catalysts.

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