

Selective lithiation and crystal structures of G1-carbosilane dendrimers with dimethoxybenzene functionalities

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Received 19 November 2003; accepted 29 December 2003

Abstract

Synthetic routes for the following dendrimers are described: $\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{CH}_2\text{-3,5-(MeO)}_2\text{-C}_6\text{H}_3]_4$ (**2**) and $\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{-2,4-(MeO)}_2\text{-C}_6\text{H}_3]_4$ (**4**). The crystal structures of these dendrimers have been determined by single crystal X-ray diffraction. One of the dendrimers (**2**) shows crystallographic S_4 -symmetry and intramolecular C–H···O bonding, whereas the other (**4**) shows crystallographic C_2 -symmetry and is imbedded in a zipper-like network of intermolecular C–H···O bonds. Direct lithiation of these dendrimers with *n*-BuLi in Et₂O yields complete and selective lithiation in the aryl ring between the methoxy substituents. However, dendrimer **2** is also partially lithiated in the benzylic group. For the solid state structure of such lithiated dendrimers, a diamond-type assembly is predicted.

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Keywords: Dendrimers; Lithium; Hydrogen bonds; Crystal engineering; Carbosilanes

1. Introduction

The last decade has seen enormous activity in the chemical research on dendritic molecules [1–6]. The driving force for the syntheses of such highly controlled molecular architectures undoubtedly is their potential for a large variety of applications [7–18]. One such application is in homogeneous catalysis using dendrimers containing transition metal chain-ends [10–16]. Dendrimers with selectively lithiated chain-ends can be used in the syntheses of metal-containing dendritic systems [19–21]. The high reactivity of organolithium reagents assures complete functionalization, a prerequisite in dendrimer syntheses. Also, the versatility of lithium reagents in organic as well as organometallic syntheses contributes to the enormous potential of dendrimers in which the chain-ends can be lithiated selectively. In continuation of our recent work on lithiated dendrimers

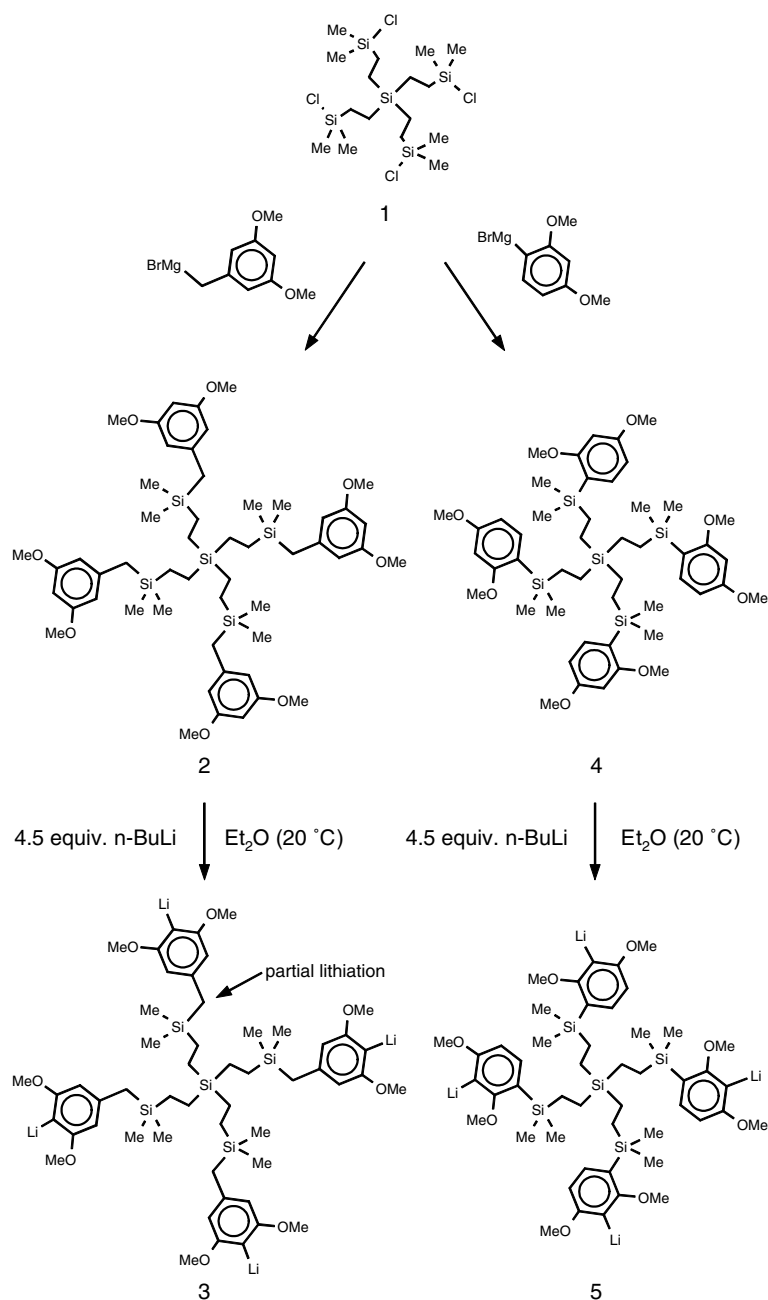
[21], we here describe the syntheses and crystal structure of two G1-dendrimers with methoxy-substituted aryl groups on its surface. The presence of these functionalities allows a selective and smooth lithiation of the dendrimer arms.

2. Results and discussion

Dendrimer **2** was prepared by reaction of the chlorocarbosilane **1** with the appropriate Grignard reagent (Scheme 1). It was recrystallized from pentane to give the required product in the form of very fine needles (yield: 51%). Since there are only a few structures of carbosilane dendrimers [22–26], we attempted a crystal structure determination of the very fine needles of **2**. The crystallographically S_4 -symmetric molecule is depicted in Fig. 1. All bond distances and angles are in the normal range (selected bond lengths and angles are shown in Table 1). One of the MeO-substituents is disordered over two positions C12a/C12b in a ratio of 72:28. The other ordered MeO-substituent is involved in a short non-classical C–H···O hydrogen bond with a Si–CH₃

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Scheme 1.

group of a neighbouring arm: $\text{H}\cdots\text{O}=2.500\text{ \AA}$, $\text{C}\cdots\text{O}=3.433(5)\text{ \AA}$ and $\text{C-H}\cdots\text{O}=145.9^\circ$. No intermolecular $\text{C-H}\cdots\text{O}$ contacts shorter than 2.60 \AA were found. Although the arms of the dendrimer extend in tetrahedral directions, the overall shape of the molecule is not spherical but more or less that of a disc with a thickness of circa 6 \AA and a diameter of circa 15 \AA . This is probably due to the formation of the intramolecular $\text{C-H}\cdots\text{O}$ hydrogen bonds and is in agreement with an earlier observation that amphiphilic dendrimers usually have structures far from spherical [27]. The discs of **2** are

perfectly stacked along the crystallographic fourfold inversion axis.

Dendrimer **2** was lithiated using the high-yield procedure for the selective deprotonation of 1,3-dimethoxybenzene in the 2-position [28], i.e., with *n*-BuLi in Et₂O at room temperature. On addition, the reaction mixture immediately went yellow–orange and a clear gel was formed. After several hours, a yellow–orange air-sensitive powder precipitated. The appearance of the yellow–orange colour is indicative of benzylic lithiation. The product was insoluble in THF and also in other

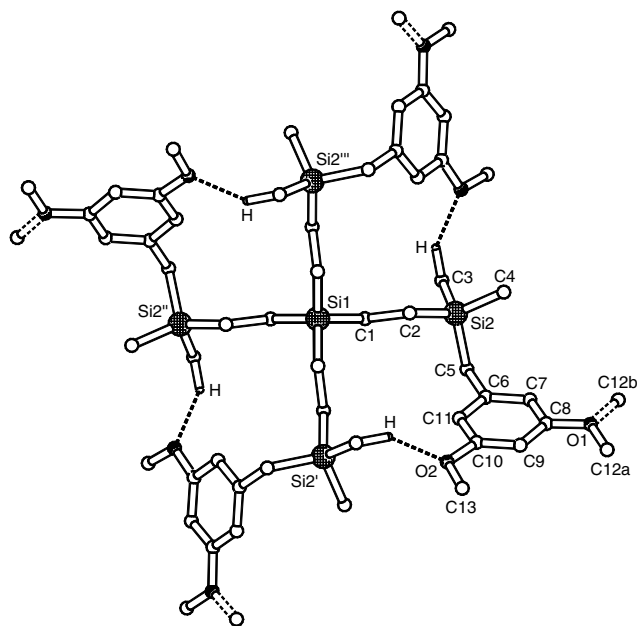


Fig. 1. Crystal structure of **2** (only the hydrogen atom involved in the C–H...O hydrogen bridge is shown). The fourfold inversion axis through Si1 is perpendicular to the plane of projection. Atom C12 is disordered over two positions C12a and C12b in a ratio of 70:30.

Table 1
Selected bond distances (Å) and angles (°) for **2** and **4**

<i>Compound 2:</i>			
Si1–C1	1.876(4)	O2–C13	1.420(6)
Si2–C2	1.884(4)	C1–C2	1.542(5)
Si2–C3	1.862(4)	C5–C6	1.496(6)
Si2–C4	1.854(5)	C6–C7	1.395(6)
Si2–C5	1.885(4)	C6–C11	1.384(6)
O1–C8	1.387(5)	C7–C8	1.391(7)
O1–C12a	1.459(8)	C8–C9	1.389(7)
O1–C12b	1.49(2)	O2–C10	1.358(6)
C9–C10	1.380(6)	C10–C11	1.398(6)
C1–Si1–C1'	112.2(2)	Si1–C1–C2	118.1(3)
C1–Si1–C1''	104.1(2)	Si2–C2–C1	115.7(3)
<i>Compound 4:</i>			
Si1–C1	1.863(6)	Si3–C13	1.869(6)
Si2–C2	1.873(6)	Si1–C14	1.866(6)
Si2–C3	1.879(7)	Si3–C15	1.862(6)
Si2–C4	1.864(7)	Si3–C16	1.863(6)
Si2–C5	1.873(6)	Si3–C17	1.878(6)
O1–C8	1.371(10)	O3–C20	1.366(7)
O1–C12	1.424(8)	O3–C23	1.446(7)

solvents compatible with a C–Li functionality. NMR analysis of the product quenched with CH₃OD showed complete deuteration in the aryl groups between the MeO-substituents and, therefore, suggested that lithiation in the aryl group had taken place selectively. However, as suspected on basis of the product colour, also partial lithiation (circa 15%) of the benzylic CH₂-group was observed by the appearance of CH₂ and CHD groups in ¹H and ¹³C NMR spectra. Even lithiation of the dendrimer with exact stoichiometric

amounts of *n*-BuLi resulted in the formation of a yellow–orange reaction mixture and partial benzylic lithiation. The lack of selectivity in the lithiation step

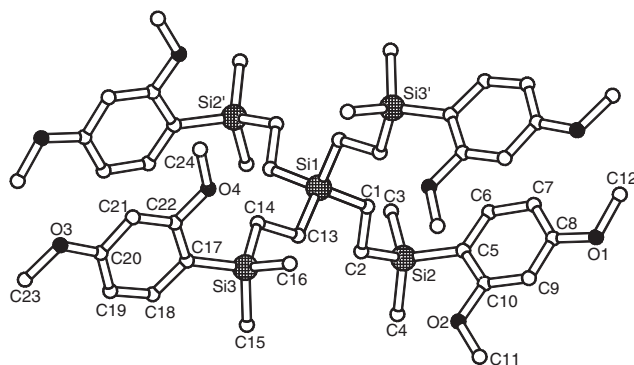


Fig. 2. Crystal structure of **4** (all hydrogen atoms have been omitted for clarity).

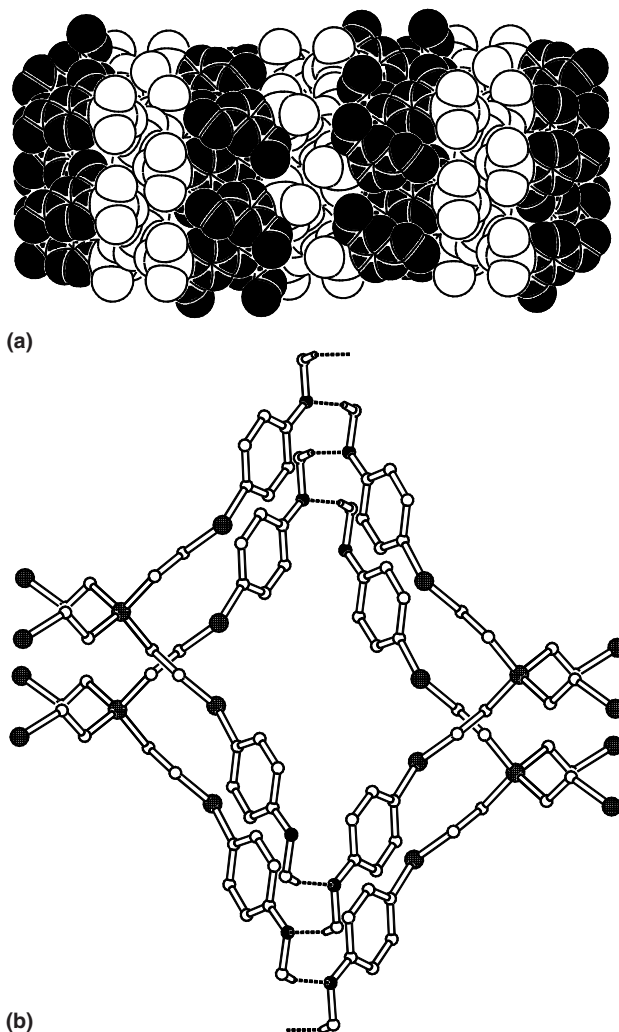


Fig. 3. Crystal packing for **4**. (a) Layers of SiCH₂CH₂Si units (white) alternated with layers of polar dimethoxyaryl substituents (black). (b) The parallel linear C–H...O–C–H...O–C–H...O hydrogen bond networks within the layer of dimethoxyaryl substituents.

spurred us to prepare a dendrimer without acidic benzylic protons.

Dendrimer **4** was prepared by reaction of the chlorocarbosilane **1** with the appropriate Grignard reagent (Scheme 1) and obtained in the form of colourless crystals. Slow crystallization from a diethyl ether solution gave **4** in the form of very thin needle-like crystals (yield: 60%). Although the crystals were small ($0.05 \times 0.1 \times 0.5 \text{ mm}^3$), sharp well-formed reflections allowed measurement up to $\theta = 20.0^\circ$ and a determination of the crystal structure. The crystallographically C_2 -symmetric structure of **4** is shown in Fig. 2. All Si-CH₂-CH₂-Si units crystallize as anti-rotamers. Bond lengths and angles are in the expected range (selected bond lengths and angles are shown in Table 1). The packing of dendrimer **4** in the crystal is shown in Fig. 3. No significant intramolecular C-H...O hydrogen bonds are observed, however, intermolecular interactions between the dimethoxybenzene substituents lead to a crystal packing that consists of two-dimensional layers of polar dimethoxybenzene parts alternated with layers of apolar carbosilane groups (Fig. 3(a)). Neighbouring dimethoxybenzene groups are bonded through non-classical C-H...O hydrogen bridges [29–32] (Fig. 3(b)): H...O = 2.353 Å, C...O = 3.406(8) Å and C-H...O = 164.6°. The hydrogen bond network consists of parallel one-dimensional chains C-H...O-C-H...O-C-H...O spanning the two-dimensional layers of dimethoxybenzene units. These zipper-like chains are comparable to the extensive networks of cooperative O-H...O-H...O-H bonds observed in alcohols or in water [33–36].

Dendrimer **4** was lithiated according to the high-yield procedure for the selective deprotonation of 1,3-dimethoxybenzene in the 2-position [28], i.e., with *n*-BuLi in Et₂O at room temperature. The extremely air-sensitive diethyl ether free lithium complex (**5**) is insoluble in THF or in any other solvent compatible with a C-Li functionality. This precludes crystallization of the product as well as NMR analyses in solution. Complete lithiation was confirmed by quenching the complex in CH₃OD and analyses of the product by NMR spectroscopy. The lithiation of **4** is complete (>99%) and proceeded selectively in the aryl ring between the MeO-substituents.

Attempted crystal growth of the lithiated product (**5**) was hindered by its insolubility in inert polar solvents, which is likely to be a result of its polymeric structure. This is a general problem of dendrimers lithiated at the periphery [19–21] (only “inner sphere” lithiated dendrimers possess C-Li functionalities that are screened from intermolecular interaction and do not aggregate) [37]. The insolubility of the lithiated dendrimer precludes crystal growth and therefore single crystal structure determination, however, we predict a three-dimensional diamond-type structure. The lithiated dendrimer **5** consists of a tetrahedral Si-center with four lithiated arms that likely form a tightly bound tetrameric aggregate with S_4 -symmetry as is observed in the crystal structure of 1,3-dimethoxy-2-lithio-benzene [38,39]. The combination of two tetrahedrally surrounded building-blocks would lead to a diamond-type assembly (Fig. 4). The junctions in the diamond structure are formed by tetrahedrally surrounded Si atoms alternated with terdentate tetrameric organolithium aggregates.

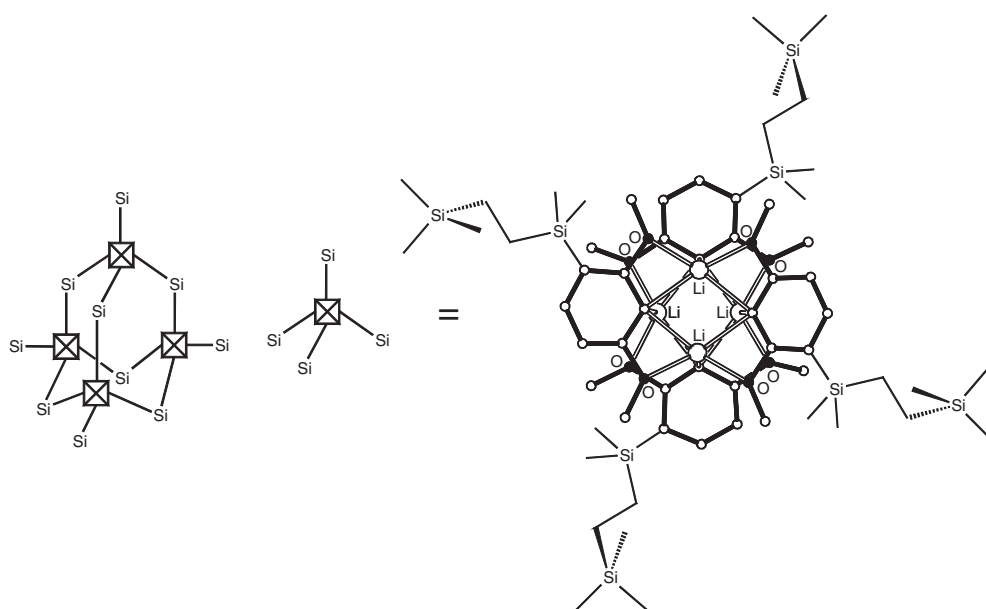


Fig. 4. Proposed diamond structure for the lithiated dendrimer **5**.

3. Conclusion

In summary, two dendritic carbosilanes with dimethoxyaryl end groups have been prepared and their crystal structures have been determined by X-ray diffraction. One of the dendrimers (**2**) shows crystallographic S_4 -symmetry and intramolecular C–H \cdots O bonding, whereas the other (**4**) shows crystallographic C_2 -symmetry and is imbedded in a zipper-like network of intermolecular C–H \cdots O bonds. Lithiation of **2** is not completely selective as deprotonation in benzylic positions is also observed. Compound **4**, however, can be completely lithiated selectively in the aryl ring between the MeO-substituents. Although **4** is a G1-dendrimer, we believe that the concept can be transferred to larger dendrimers.

4. Experimental

4.1. General procedures

All experiments were carried out under argon using predried solvents and Schlenk techniques. The following chemicals were purchased: *n*-BuLi (Chemmetal), α -bromo-3,5-dimethoxytoluene (Aldrich) and 1-bromo-2,4-dimethoxybenzene (Aldrich). The carbosilane chloride **1** was prepared according to a literature procedure [40]. NMR spectra were recorded on Varian Unity-400 and JEOL JNM-GX400 spectrometers. Chemical shifts were referenced to TMS using either the residual protio impurities in the solvent (^1H NMR), the solvent resonances (^{13}C NMR) or with an external standard (^{29}Si NMR). Elemental analyses were done with a CHN-analyzer (C–H–N–O–RAPID, Leybold-Heraeus). FAB-mass spectra were measured on a MAT312/AMD5000 (Finnigan). Crystal data were collected on an Enraf-Nonius CAD4 four-cycle diffractometer. The selected crystal was layered with paraffin oil and transferred in a cold nitrogen stream (-90°C or -120°C). Crystal structures were determined with the programs SHELXL-97 [41] and PLATON [42]. For the determination of the C–H \cdots O hydrogen bond geometries, the hydrogens were placed on realistic positions with C–H distances of 1.08 Å.

4.2. Synthesis of dendrimer 2

A solution of α -bromo-3,5-dimethoxytoluene (2.31 g, 10.0 mmol) in diethyl ether (20 ml) was slowly added to Mg chips (0.75 g, 30.9 mmol, activated with 1,2-dibromoethane) in diethyl ether (10 ml). The reaction mixture started to reflux. After complete addition of the bromide (30 min), the reaction mixture separated in two layers. The mixture was refluxed for 10 min and, after cooling to room temperature, THF (50 ml) was added. This resulted in complete dissolution of the Grignard.

The Grignard solution was added to a precooled (-70°C) solution of **1** (0.74 g, 1.44 mmol) in THF (10 ml) and the temperature of the cooling bath was allowed to rise slowly to room temperature overnight. The solvents contained in the resulting grey solution were removed under vacuum after which water (20 ml) was added. The aqueous layer was carefully acidified with HCl (pH 4–5) and extracted with diethyl ether (3×20 ml). The raw product was purified by column chromatography (neutral alumina oxide, pentane/ethyl acetate 95/5 eluant). The crude product was recrystallized from pentane and obtained as colourless needles (0.71 g, 0.73 mmol, 51%). ^1H NMR (CDCl_3 , 20°C): δ -0.04 (s, 24 H, SiMe_2), 0.30 – 0.43 (m, 16 H, CH_2CH_2), 2.02 (s, 8 H, SiCH_2Ar), 3.73 (s, 24 H, OMe), 6.15 (d, 2.1 Hz, 4 H, aryl), 6.18 (t, 2.1 Hz, 4 H, aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 20°C): δ -4.1 (SiMe_2), 2.7 (CH_2), 7.1 (CH_2), 25.5 (SiCH_2Ar), 55.1 (OMe), aryl: 95.8 , 106.3 , 142.9 , 160.5 . $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 20°C): δ -3.98 (Si_{aryl}) 1.12 (Si_{core}). FAB-MS, m/z : 1001 [$\text{M}^+ + \text{Na}$]. Elemental anal. calcd. (%) for $\text{C}_{52}\text{H}_{84}\text{O}_8\text{Si}_5$ (977.58): C 63.88, H 8.66. Found: C 63.65, H 8.80.

4.3. Synthesis of dendrimer 4

A solution of 1-bromo-2,4-dimethoxybenzene (6.50 g, 29.9 mmol) in diethyl ether (50 ml) was slowly added to Mg chips (2.50 g, 10.2 mmol, activated with 1,2-dibromoethane) in diethyl ether (30 ml). The reaction mixture started to reflux. After complete addition of the bromide (30 min), the reaction mixture was refluxed for 10 min. The Grignard solution was added to a precooled (-40°C) solution of **1** (1.90 g, 3.69 mmol) in THF (25 ml) and the temperature of the cooling bath was allowed to rise slowly. At room temperature, a white precipitate of magnesium salts was formed and the suspension was refluxed for 4 h. The crude product consisted of two compounds and was purified by column chromatography (neutral alumina oxide, pentane/ethyl acetate (95/5) eluant). The product **4** was isolated as an oil that crystallized overnight (2.04 g, 2.21 mmol, 60%). ^1H NMR (CDCl_3 , 20°C): δ 0.19 (s, 24 H, SiMe_2), 0.35 – 0.63 (m, 16 H, CH_2CH_2), 3.68 (s, 12 H, OMe), 3.80 (s, 12 H, OMe), 6.37 (d, 2.0 Hz, 4 H, aryl), 6.46 (dd, 8.0 and 2.0 Hz, 4 H, aryl), 7.24 (d, 8.0 Hz, 4 H, aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 20°C): δ -3.9 (SiMe_2), 3.0 (CH_2), 7.6 (CH_2), 54.9 (OMe), 55.1 (OMe), aryl: 97.6 , 104.2 , 118.6 , 136.1 , 162.2 , 165.7 . $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 20°C): -4.09 (Si_{aryl}) 0.80 (Si_{core}). FAB-MS, m/z : 944 [$\text{M}^+ + \text{Na}$]. Elemental anal. calcd. (%) for $\text{C}_{48}\text{H}_{76}\text{O}_8\text{Si}_5$ (921.54): C 62.56, H 8.31. Found: C 62.41, H 8.39.

4.4. Lithiation of dendrimer 4

A solution of **4** (0.68 g, 0.74 mmol) in diethyl ether (8 ml) was reacted with 4.5 equivalents of *n*-BuLi (3.36

mmol, 2.1 ml of a 1.6 M solution in hexane) for 48 h. During the course of the reaction, a white precipitate was formed. Evaporation of all solvent yielded a white powder that is completely insoluble in THF. Complete (>99%) lithiation of **4** was confirmed by deuteration of the lithium compound with CH₃OD and analyses of the product. ¹H NMR (CDCl₃, 20 °C): δ 0.19 (s, 24 H, SiMe₂), 0.35–0.63 (m, 16 H, CH₂CH₂), 3.68 (s, 12 H, OMe), 3.80 (s, 12 H, OMe), 6.46 (d, 8.0 Hz, 4 H, aryl), 7.24 (d, 8.0 Hz, 4 H, aryl). ¹³C{¹H} NMR (CDCl₃, 20 °C): δ -3.9 (SiMe₂), 3.0 (CH₂), 7.57 (CH₂), 54.9 (OMe), 55.1 (OMe), aryl: 97.4 (t, ¹J(C,D) = 22.6 Hz), 104.2, 118.6, 136.1, 162.2, 165.7. FAB-MS, *m/z*: 948 [M⁺ + Na]. Elemental anal. calcd. (%) for C₄₈H₇₂D₄O₈Si₅ (921.54): C 62.29, H 7.84. Found: C 62.02, H 7.98.

4.5. Crystal data for dendrimer **2**

Slow cooling of a solution of **2** in pentane yielded colourless needle-like crystals of which one (0.1 × 0.1 × 0.5 mm³) was used for X-ray diffraction. Crystal data: tetragonal, *a* = *b* = 21.290(3), *c* = 6.1815(15) Å, *V* = 2801.9(9) Å³, space group *I*-4; formula (C₅₂H₈₄O₈Si₅), *M* = 977.64, *Z* = 2, ρ_{calcd} = 1.159 g cm⁻³, μ(Mo Kα) = 0.176 mm⁻¹; 2900 reflections (θ-range 0–24.0°) were measured (Mo Kα = 0.71073 Å, graphite monochromator, *T* = -120 °C), 2491 independent reflections, 2130 observed reflections with *I* > 2.0 σ(*I*). Full matrix least-squares refinement on *F*₂ to *R*₁ = 0.049, *wR*₂ = 0.013 and *S* = 1.07 (162 refined parameters, maximum and average shift errors were smaller than 0.001, minimum and maximum residual electron densities are -0.25 and +0.40 e Å⁻³). All hydrogens were positioned on calculated positions and refined with a riding model and free isotropic displacement factors. One of the MeO-substituents is disordered over two positions C12a/C12b in a ratio of 70:30.

4.6. Crystal data for dendrimer **4**

Concentration of a solution of **4** in diethyl ether by slow evaporation over several months time yielded colourless needle-like crystals of which one (0.05 × 0.1 × 0.5 mm³) was used for X-ray diffraction. Crystal data: orthorhombic, *a* = 7.3510(8), *b* = 27.863(3), *c* = 25.992(2) Å, *V* = 5323.7(9) Å³, space group *Pnna*; formula (C₄₈H₇₆O₈Si₅), *M* = 921.54, *Z* = 4, ρ_{calcd} = 1.150 g cm⁻³, μ(Mo Kα) = 0.181 mm⁻¹; 4794 reflections (θ-range 0–20.0°) were measured (Mo Kα = 0.71073 Å, graphite monochromator, *T* = -120 °C), 2432 independent reflections, 1477 observed reflections with *I* > 2.0 σ(*I*). Full matrix least-squares refinement on *F*₂ to *R*₁ = 0.052, *wR*₂ = 0.086 and *S* = 0.99 (284 refined parameters, maximum and average shift errors were smaller than 0.001, minimum and maximum residual electron densities are -0.21 and +0.17 e Å⁻³). All hydrogens were

positioned on calculated positions and refined with a riding model and free isotropic displacement factors.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **2** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-214326 and CCDC-214327, respectively. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We are grateful to the University of Cape Town and the Universität Konstanz for enabling this research project; we thank NRF for financial support. S.H. thanks the DFG (Germany) for a travel bursary to visit South Africa.

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