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Tetra-functional double-decker silsesquioxanes as anchors for reactive functional groups and potential synthons for hybrid materials[†]

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A series of double-decker silsesquioxane derivatives with four reactive functional groups were designed, efficiently synthesized, and characterized. These novel inorganic-organic hybrids show highly attractive features for applications as building blocks with Si-O-Si rigid cores (good thermal properties) with four reactive moieties, which can be functionalized in further processes.

The development of novel materials with specially designed and tailored chemical, mechanical, or physical properties has become increasingly important to meet the various requirements and expectations of applications in many fields of science and everyday life. Polyhedral oligomeric silsesquioxanes are a broad family of compounds known for a large variety of structures. Their structures may vary from random, ladder, open, and incompletely condensed species to closed and well-defined cages. The POSS general formula is $[RSiO_{1.5}]_n$ (where R = H, alkyl, aryl, *etc.* and n = 4, 6, 8, 10...). Their main components are cubic T₈ cages consisting of rigid, crystalline silica-like cores with eight covalently bonded R groups (either the same or different functional groups (FGs)).¹⁻³ Another type of silsesquioxane structure is a double-decker silsesquioxane (DDSQ – M_4T_8 and D_2T_8), whose efficient synthesis was reported by Yoshida et al. just over a decade ago.⁴⁻¹⁰ The structure of DDSQ differs from those of symmetric, cubic T8 systems. It consists of two "decks" of cyclosiloxane rings stacked on top of one another with four inert phenyl groups at the silicon atoms of each ring. The rings are joined by oxygen bridges. DDSQ compounds may take an open M₄T₈ (DDSQ-2OSi)^{6,7} or closed D₂T₈ (DDSQ-4OSi)^{9,10} framework with either four or two reactive groups, respectively,

and the chemistry of these compounds is considerably dependent on the type and number of functional groups (Scheme 1).

Research on molecular and macromolecular organosilicon DDSQ-based systems is developing in two directions. Molecular derivatives based on DDSQ are interesting from a purely cognitive point of view, related to syntheses of compounds with interesting physicochemical properties. In contrast, they can be precursors and reagents in the synthesis of oligo- and polymeric networks.¹¹ The number of examples of D₂T₈-closed architectures has increased recently. Not only have hydrolytic condensation reactions been applied to their syntheses, but catalytic reactions of di-functional DDSQ-based compounds with reactive FG vertex groups have also been used in their syntheses. Ervithayasuporn et al.,¹²⁻¹⁴ Lee et al.,¹⁵⁻¹⁸ and our group have made significant contributions to the studies on geometric cis- and trans-DDSQ-2Si isomers whose formation is related to the different spatial arrangements of the FG and R substituents on the DDSQ core.¹⁹⁻²² A skillful selection of solvents based on the differences in the solubilities of the isomers, e.g., THF/hexane, enables their efficient separation via fractional crystallization. The main idea behind the introduction of two FGs into the DDSQ core was the potential to use these new systems as precursors for the synthesis of macromolecular compounds with DDSQ as a linker or a fragment incorporated into the copolymer chain. The consecutive processes



Scheme 1 Double-decker silsesquioxane derivatives – possible structures.

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leading to co-polymeric materials are based on organic/ organometallic-type transformations with FGs at the Si vertex (DDSQ) and organic, di-functional co-monomers, e.g., dehydrocoupling polycondensation, nucleophilic substitution, hydrosilvlation, metathesis, and silvlative coupling.^{11,20,21,23-28} As a result, an interesting group of compounds has been designed and prepared over the last few years. They have been found to exhibit interesting mechanical and optical properties, offer low dielectric constants, and above all, high thermal stability. In contrast, the number of scientific reports on the synthesis of tetra-functional double-decker-based molecular compounds (DDSQ-4Si) is still limited. A few reports on tetra(N-ethylcarbazole) DDSO derivatives applied in OLED (organic light-emitting diode) devices²⁹ or ethylene glycol-based DDSQ compounds with interesting proton conductivity properties have been published thus far.^{30,31} Further, the tetrasilanol form of DDSQ (DDSQ-4OH) has been used as a ligand scaffold for a Zr complex³² or as a co-monomer in the formation of macromolecular DDSO systems with titanium(IV) atoms as the nodes.³³

Herein, we present an efficient synthesis of tetra-functional DDSQ compounds with a few FGs, *i.e.* Si–H, Si–alkene and Si–C \equiv CH that are particularly interesting, *e.g.*, for the syntheses of polymers or their modification or as new types of cores for specific types of dendritic systems, *i.e.*, playing the role of the core for dendrons arising at four independent branches. Their structures were analyzed using a variety of spectroscopic methods (also XRD for **1-Me**, **2-Me**, and **4-Me**). Further, the thermal properties of these compounds were measured and compared with those of known DDSQ-based derivatives.

The synthetic importance of tetra-functional DDSQ-based compounds as building blocks for hybrid materials of both molecular and macromolecular architectures may be even greater than that of di-functional DDSQ. This opens a route for the design and synthesis of novel types of inorganic–organic DDSQ-based systems. The type of FG attached to the core plays a decisive role in planning the reaction strategy.

The fundamental process that leads to tetra-functional double-decker silsesquioxanes is the hydrolytic condensation of the commercially available tetrasilanol (DDSQ-4OH) with dichloro (or dialkoxy) functionalized silanes.^{11,23} The syntheses of **1–5** were performed as per Scheme 2. The condensation reactions were optimized enabling the highest conversions of DDSQ-4OH. This process involves the verification of the reagent stoichiometry, reaction times, and amounts of solvent. For effective



Scheme 2 Reaction pathway for the synthesis of tetra-functional DDSQ derivatives.

product formation, the respective silane should be used in 1.05 equiv. per Si-OH moiety. THF was chosen as the best solvent because of the solubility of DDSQ-4OH; NEt₃ was chosen as the base and HCl the scavenger. We tested a few types of bases, e.g., K₂CO₃ and N(iPr)₂Et, but NEt₃ was the most efficient. The reaction time depended on the reagent concentrations in THF and was monitored using 29Si NMR for the disappearance of Si-OH resonance lines, usually up to 24 h (see Fig. S4 in ESI⁺). The crude reaction mixture was purified by filtration from the [HNEt₃]Cl salt. Then, either recrystallization in MeOH was performed to afford 1-Me, 1-Ph, and 2-Ph or column chromatography was performed for 3-Me, 5-Me-hex, and 5-Me-dec with high yields of 68-95%. The solubility of 2-Me and 4-Me in MeOH was observed to be significantly higher than that of the other compounds (which might be explained by the different polarities of these molecules, possibly due to the changed electronic effects of the vinyl and ethynyl groups).

This process not only allowed a thorough purification of these compounds but also made it possible to obtain crystals for single crystal XRD studies. The condensation of **5-Me** was ineffective, probably because of the steric hindrance of chloro(1-decenyl)- and chloro(1-hexenyl)dimethylsilane and resulted in incomplete Si–OH consumption (²⁹Si NMR analysis). This was also reflected by the relatively low yield of **3-Me**. Consequently, we decided to explore another reaction pathway to obtain the desired product **5-Me**.

The tetrahydro-functional DDSQ derivative 1-Me served as a substrate in hydrosilylation, using commercially available Pt-Karstedt's catalyst $[Pt_2(dvs)_3]$ and a corresponding diene, i.e., 1,5-hexadiene and 1,9-decadiene. A particular amount of catalyst was used to ensure the proportion of 10^{-4} mole of Pt per mole of the Si-H group. The reaction was monitored by following the disappearance of the bands at \bar{v} = 2100 and 903 cm⁻¹, originating from the stretching and bending vibrations of the Si-H group (Fig. S5 in ESI⁺). The reaction conditions enabled > 99% Si–H conversion and selective formation of the β -product (Scheme 2). The crude products were purified from the catalyst using column chromatography with a DCM: hexane (3:2) eluent, and its evaporation yielded analytically pure compounds with very high isolation yields of 93-94%. All the products were characterized using spectroscopic methods. The results of the ²⁹Si NMR analysis are presented in Table 1.

The location of the resonance lines of the Si atoms derived from the rigid Si–O–Si core (\diamond) was not affected much by the presence of FGs, but the chemical shifts of the four Si atoms from external Si–O– groups (\bigcirc) were changed decisively (because of the differences in the electronic effects of the substituents at the M type Si). The Ph groups' vicinity to the Si–O– groups (\bigcirc) in **1-Ph** and **2-Ph** affects the location of the ²⁹Si NMR chemical signals of Si atoms (\bigcirc) predominantly (the resonance lines are shifted to –45.5 ppm for **1-Ph** and to –20.3 ppm for **2-Ph**) when compared with the shifts observed for their Me derivatives. For **3-Me**, **5-Me-hex**, and **5-Me-dec**, the resonance lines of the M-type Si atoms are shifted toward positive ppm values (lower field) because of the presence of the Me– group and additional –CH₂– (C_{sp3}) moieties of alkenyl groups.

$\begin{array}{c} Ph & Ph & R_2 \\ R_2 & Ph & O & O & O \\ FG & Sh & O & O & Sh & FG \\ FG & Sh & O & Sh & Ph & R_2 \\ R_2 & R_2 & Ph & O & O & O & Sh \\ FG & Sh & O & O & O & O \\ FG & Sh & O & O & O & O \\ R_2 & R_2 & Ph & O & O & O \\ R_2 & Ph & O & O & O & Ph \\ R_2 & Ph & O & O & O & Ph \\ R_2 & Ph & O & O & O & Ph \\ R_2 & Ph & O & O & Ph \\ R_2 & Ph & O & O & Ph \\ R_2 & Ph & O & O & Ph \\ R_2 & Ph & O & O & O \\ Sh & Sh \\ Sh & O \\ Sh & Sh \\ Sh & O \\ Sh & Sh \\ Sh & Sh & Sh \\ Sh & Sh \\ Sh & Sh & Sh \\ Sh \\ Sh & Sh \\ Sh & Sh \\ Sh \\ S$					
Prod. abbrev.	²⁹ Si NMR resonance lines [ppm] in CDCl ₃				
1-Me	-3.9 (○), -75.8 (◊), -79.0 (◊)				
1-Ph	-45.4 (○), -78.1 (◊), -79.4 (◊)				
2-Me	-0.8 (\bigcirc), -75.9 (\diamondsuit), -78.9 (\diamondsuit)				
2-Ph	-20.3 (\bigcirc), -76.2 (\diamondsuit), -77.7 (\diamondsuit)				
3-Me	7.9 (○), -75.8 (◊), -78.7 (◊)				
4-Me	-16.5 (O), -75.8 (\Diamond), -78.6 (\Diamond)				
5-Me-hex	10.9 (○), -76.2 (◊), -78.8 (◊)				
5-Me-dec	11.0 (○), -76.1 (◊), -78.7 (◊)				
Type of Si atom: M 🔾 (-Si-	O–) and T ♦ (–Si(O–) ₃)				



Fig. 1 Perspective view of the molecule **1-Me**. Ellipsoids are drawn at the 50% probability level.

We succeeded in obtaining crystal structures of three of the synthesized compounds, *i.e.*, **1-Me**, **2-Me**, and **4-Me**. The perspective views of the molecules are presented in Fig. 1–3. The molecule **1-Me** is C_i -symmetrical, as it lies at the inversion center in the space group $P\overline{1}$. Even though **2-Me** is not exactly symmetrical, the overall shapes and disposition of the substituents in both molecules are quite similar (Fig. 4). The geometrical features are quite typical; one can infer that the Si–O bond lengths of SiO₃C (mean values of 1.618(7) Å in **2-Me** and



Fig. 2 Perspective view of the molecule **2-Me**. Ellipsoids are drawn at the 35% probability level.



Fig. 3 Perspective view of the molecule **4-Me**. Ellipsoids are drawn at the 35% probability level.



Fig. 4 Comparison of the shapes of molecules (left) **1-Me** (red) and **2-Me** (green), and (right) **2-Me** and **4-Me** (blue).

1.614(8) Å in **1-Me**) differ slightly from those of the SiOC₃ grouping in which these bonds are significantly longer (1.644 and 1.639 Å). The Si–O–Si bond angles are considerably more flexible and have values ranging from 135° to 155°. In the crystal structures, the van der Waals forces organize molecules into three-dimensional networks (Fig. S1–S3 in ESI†).

Subsequently, all obtained samples 1-5 were subjected to thermogravimetric studies. The analysis of the obtained thermograms led to the conclusion that all the compounds show relatively high thermal resistance $T_d^{5\%}$ (all over 350 °C in N_2 and 290 °C in air) with a residue at 1000 °C of up to 58% in N₂ and 45% in air (Table 2). TGAs of compounds 1-5 (Fig. S6 and S7 in ESI[†]) show general information about the thermal stability of these systems. Here, the final residues' mass values at 1000 °C (within the range of 22% to 58% in N2 and air respectively) may not reflect the mass loss caused by the process other than decomposition (*i.e.*, sublimation, volatilization or evaporation).² It is hard to make a direct correlation between the thermal stability and structure/composition without additional analysis to account for the mass loss by these other processes. However, the theoretical yields of SiO₂ in air were calculated within the range of 38% for 2-Ph and 5-Me-hex to 55% for 1-Me, respectively. The lower residue values may be attributed to possible sample sublimation.² In general, the presence of a Me or Ph substituent at the M-type Si-O- moiety may be reflected by the difference in the $T_{\rm d}^{5\%}$ and $T_{\rm d}^{10\%}$ temperatures (higher for Ph derivatives in N2 and air) (Table 2). DDSQ-4OSi-FGs are characterized by different 5% and 10% mass loss temperatures compared to the analogous DDSQ-4OSi-based systems, which

Table 2 Thermal properties of DDSQ-4OSi-FG (1–5) (measured in N_2 and air)

Prod. abbrev.	Mass loss temperature (°C)				Residue at 1000 °C (%)	
	5% (N ₂)	5% (in air)	10% (N ₂)	10% (in air)	(N_2)	(In air)
1-Me	351	331	373	358	37	30
1-Ph	390	344	428	399	24	22
2-Me	400	361	429	379	37	37
2-Ph	423	377	456	412	31	37
3-Me	362	297	397	378	34	45
4-Me	373	347	440	377	58	43
5-Me-hex	404	400	427	433	31	22
5-Me-dec	426	361	457	425	31	30

may be attributed to the differences in the FGs.^{29,30} In the case of **4-Me**, the final residue was at 58%.

The presence of –CCH moieties may suggest their possibility to undergo an intermolecular thermal coupling reaction to yield a co- or polymeric material. A similar observation was reported by Kawakami *et al.*, in the study of the TGA of DDSQ-4OH. In their case, the intermolecular thermal condensation was noted as a probable explanation of this phenomenon.³⁴ The issue of the potential decomposition mechanism of these compounds as well as the discrepancies in the final residue values of samples **1–5** will be a subject of our further detailed research. This may also require more complete analyses, *e.g.*, of exhaust gasses emitted from the degradation of the material (by TGA-MS or TGA-IR) or performing the TGA with a different gas flow rate.

In summary, we have reported the design and synthesis of inorganic-organic DDSQ-based building blocks characterized by a rigid structure and the presence of four FGs, *i.e.*, -H, -HC=CH₂, -CH₂CH=CH₂, -CCH, -hex-5-enyl, and -dec-9-enyl. The new compounds were precisely characterized using spectroscopic and XRD methods, and their thermal properties were determined. These DDSQ-4OSi-FG compounds may be used as valuable precursors for the synthesis of macromolecular hybrid systems of the original architecture. They may act as nodes that contribute to the definition of a three-dimensional Si-O-Si rigid framework, responsible for the improvement of, e.g., optical, thermal, or mechanical properties of synthesized materials. The type of FG implies certain synthetic strategies and co-reagents to be used for obtaining the desired hybrid material. Our studies may open a new unexplored field of research in the chemistry of double-decker silsesquioxanes, which can lead to novel, molecular and macromolecular systems based on selectively introduced functionalities.

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Conflicts of interest

The authors have no conflicts of interest to declare for this communication.

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