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Interlinkage of a siliconoid with a silsesquioxane: en route to a molecular model system for silicon monoxide

Marc Hunsicker,^[a] Nadine E. Poitiers,^[a] Volker Huch,^[a] Bernd Morgenstern,^[a] Michael Zimmer,^[a] and David Scheschkewitz*^[a]

Dedicated to Prof. Cameron Jones on occasion of his 60th birthday.

A new potential model system for silicon monoxide (SiO) is synthesized by the interlinkage of an unsaturated silicon cluster (siliconoid) with a polyhedral silsesquioxane cage. Two derivatives with variable linker size are obtained by the corner-capping reaction of Ph₇T₇(ONa)₃ with a trichlorosilane featuring a remote benzylic chloride functionality and the subsequent

nucleophilic substitution of the latter by the anionic hexasilabenzopolarene-type Si₆ siliconoid. Based on the recently proposed heterogeneous cluster model for the SiO structure, the stoichiometry between silicon and oxygen reiterates the suboxidic interface of the nano-composite in a Si:O ratio of 14:12.

Introduction

Silicon monoxide (SiO) has been reported more than 130 years ago,^[1] yet relatively little is known about the structure of this commercially available material, which is nonetheless extensively employed, e.g. as antireflective coating.^[2d,e] More recently, it is being investigated along with suboxidic SiO_x species as a component of anode materials in lithium ion batteries^[2a–c,f,g] and as pivotal component of silicon nanowires in light-enhanced hydrogen generation.^[2h]

SiO is usually prepared by thermal evaporation of elemental Si and SiO₂. In the gas phase at high temperatures it predominantly exists as a diatomic molecule, which is subsequently condensed by cooling.^[3] Depending on the cooling rate, different modifications of SiO are obtained of which the amorphous dark powder is typically employed for the various applications.^[4] In contrast to SiO₂,^[5] the solid state structure of SiO is still a controversial subject,^[6] and is either described as a single phase^[7] or an amorphous, nanoscalar composite of Si and SiO₂.^[6,8] Earlier suggestions of a simple macroscopic mixture of Si and SiO₂^[9] are neither in line with the distinct reactivity of SiO,^[6] nor with spectroscopic findings.^[10] The random bonding model proposed by Philipp assumes a continuous network of

arbitrarily distributed covalent Si–O and Si–Si bonds.^[11] Such a network could be regarded as a single macroscopic phase of SiO, but would not account for the aforementioned thermodynamically driven disproportionation of SiO. Recently, Chen et al. developed a heterogeneous structure model consisting of elemental silicon clusters incorporated into an amorphous SiO₂ matrix with interfacial Si(Si_{4–x}O_x) tetrahedra.^[12]

In view of the lack of empirical evidence for the SiO structure, several (potential) model systems have been conceived. Ionic phases approximating the Si/O ratio of 1:1 incorporate both discrete Si-based Zintl anions and silicate anions as reported by the groups of Fässler and Röhr.^[13] In fact, SiO was suspected as byproduct of this synthesis. Molecular species with silicon suboxide motifs have been reported as well, all containing strong external donors to increase stability: Filippou et al. prepared a chromium complex of NHC-stabilized SiO,^[14] while Robinson et al. isolated several disilicon suboxides coordinated by NHC ligands.^[15]

Herein, we report the synthesis of a well-defined and stable potential molecular model system, which combines an unsaturated Si₆ siliconoid with a T₈ silsesquioxane in one and the same molecule and thus reiterates Chen's model with local molecular Si and SiO clusters.^[12] While silsesquioxanes have been suggested as models for silica surfaces and silica supported transition metal catalysts,^[16] siliconoids are implied as intermediates in gas phase deposition processes of elemental silicon^[17] and – in the form of stable molecular representatives regarded as model systems for silicon surfaces (Figure 1).^[18]

Results and Discussion

Anionically functionalized siliconoids are easily derivatized in a straightforward manner by reactions with various electrophiles, which mostly proceed without compromising the integrity of the Si₆ cluster scaffold.^[19] Yet, attempts to introduce the 4-vinylbenzoyl group (as a group potentially amenable to

[a] M. Hunsicker, Dr. N. E. Poitiers, Dr. V. Huch, Dr. B. Morgenstern, Dr. M. Zimmer, Prof. Dr. D. Scheschkewitz
Krupp-Chair of Inorganic and General Chemistry
Saarland University
66123 Saarbrücken (Germany)
E-mail: scheschkewitz@mx.uni-saarland.de

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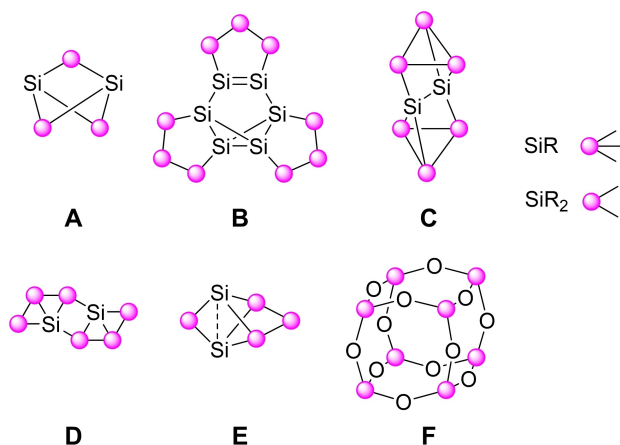
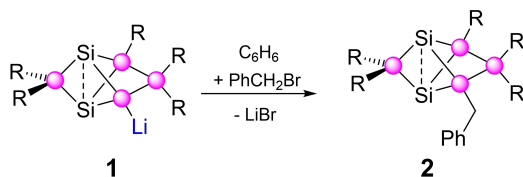


Figure 1. Selected examples of unsaturated neutral siliconoids **A** to **E**^[18] and of polyhedral molecular silsesquioxanes **F**^[16] (●: saturated silicon vertex, Si: unsubstituted silicon vertex).

subsequent hydrosilylation by T_8Ph_7H in *ligato*-position^[20] of a hexasilabenzpolarene scaffold gave complex and intractable product mixtures. Although hydro silsesquioxanes are routinely modified by hydrosilylation procedures,^[21] the reverse approach of initial grafting of the linker units to T_8Ph_7H by reaction with suitably functionalized terminal alkenes in the presence of either the Karstedt catalyst or palladium on charcoal only resulted in partial conversion of the silsesquioxane. In contrast, corner-capping reactions^[22] of incompletely condensed T_7 silsesquioxanes using highly electrophilic trichlorosilanes tolerate less reactive remote functionalities potentially amenable to later introduction of the hexasilabenzpolarene motif. In terms of grafting the substituted T_8 to the anionic *ligato* lithiated hexasilabenzpolarene **1**, we selected a remote benzylic halide functionality in *para*-position to the ethylene moiety.^[23] Encouragingly, the test reaction of the *ligato*-lithiated hexasilabenzpolarene **1** with benzyl bromide yielded the benzyl-substituted **2** in 75% isolated yield (Scheme 1).

The desired trichlorosilane **3** with remote benzylic chloride was obtained by hydrosilylation of *para*-vinylbenzyl chloride with trichlorosilane through an adapted literature procedure (see Supporting Info).^[24] In our hands, the anti-Markovnikov selectivity of the reaction heavily depended on the choice of catalyst. The use of Pt/C finally allowed for the isolation of **3** by vacuum distillation in 67% yield.

The subsequent treatment of $Ph_7T_7(ONa)_3$ with a slight excess of trichlorosilane **3** in tetrahydrofuran at 0 °C indeed



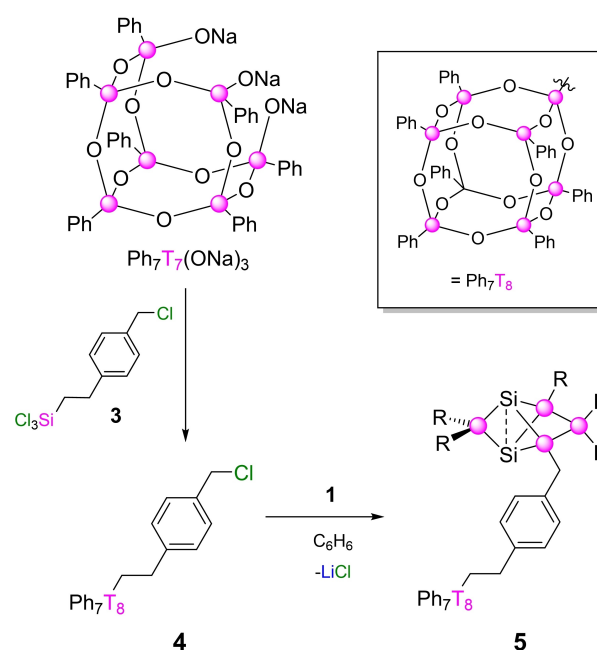
Scheme 1. Test reaction of anionic siliconoid **1** with benzyl bromide to obtain benzyl functionalized hexasilabenzpolarene.

affords the T_8 -substituted benzyl chloride **4** as a white solid in 46% yield after aqueous work-up (Scheme 2).

The ethylene moiety in **4** gives rise to characteristic 1H NMR multiplets between 2.79 and 2.75 ppm as well as 1.16 and 1.12 ppm, respectively. The ^{13}C NMR signals of the corresponding carbon atoms are observed at 28.83 and 14.14 ppm. The benzylic group gives rise to a 1H NMR singlet at 4.08 ppm and a ^{13}C NMR signal at 46.19 ppm. The ^{29}Si NMR resonances in C_6D_6 of the T_8 cage in **4** are observed at -65.4 , -77.6 and -78.0 ppm. While the local C_{3v} symmetry would demand four signals, monofunctionalized T_8 cages often only show three ^{29}Si signals due to incidental isochronism of the phenyl-substituted corners of the T_8 cage.^[25] A 1H - ^{29}Si NMR correlation experiment assigned the resonance at -65.4 ppm to the newly introduced silicon vertex (Experimental Section/SI). In contrast, the parent species T_8Ph_8 exhibits one signal at -78.3 ppm in $CDCl_3$,^[26] while silsesquioxane **4** gives rise to resonances at -65.8 , -78.3 and -78.6 ppm in this solvent.

Reaction with the anionic silicon cluster **1** in benzene at 25 °C quantitatively afforded the anticipated benzpolarene-grafted T_8 cage **5**. Crystallization from a benzene solution afforded orange crystals of **5** in 31% yield (Figure 2). Single crystals suitable for X-ray diffraction were grown from a 10:1 mixture of toluene and hexane.

The Si1–Si3 distance of the *nudo*-silicon atoms of 2.640(1) Å is at the short end of the typical range for neutral hexasilabenzpolarenes.^[19b] Despite the difference in carbon hybridization, the bond between the T_8 silicon vertex to the



Scheme 2. Corner capping reaction of the incompletely condensed heptaphenyl silsesquioxane $T_7Ph_7(ONa)_3$ with trichlorosilane **3** containing the linking group ($R = Tip = 2,4,6$ -triisopropylphenyl), as well as grafting reaction to lithiated hexasilabenzpolarene motif by nucleophilic substitution of chloride at benzylic carbon atom to yield the potential SiO model system **5**.

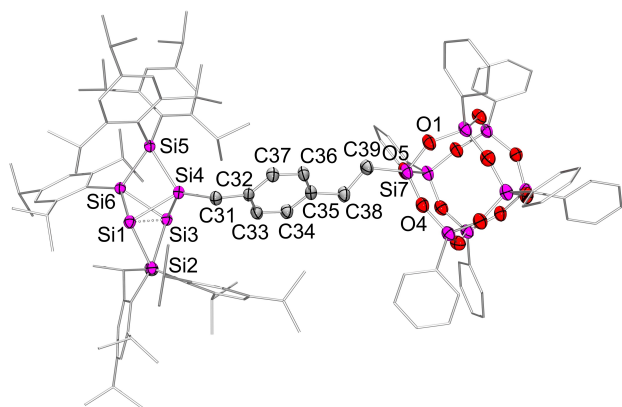


Figure 2. Molecular structure of potential SiO model system **5** in the solid state. Thermal ellipsoids at 50% probability, hydrogen atoms and co-crystallized solvent molecules omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.357(1), Si1–Si3 2.640(1), Si1–Si4 2.374(1), Si1–Si6 2.329(1), Si2–Si3 2.395(1), Si3–Si4 2.315(1), Si3–Si6 2.376(1), Si4–Si5 2.345(1), Si5–Si6 2.388(1), Si4–C31 1.894(3), C31–C32 1.513(4), C32–C37 1.384(4), C37–C36 1.393(4), C36–C35 1.381(4), C35–C38 1.512(4), C38–C39 1.514(4), C39–Si7 1.838(3); O1–Si7–O4 109.7(1), O4–Si7–O5 108.2(1), O1–Si7–O5 109.4(1), O1–Si7–C39 109.1(1), O4–Si–C39 110.2(1), O5–Si7–C39 110.3(1).

pending ethylene moiety (Si7–C39 1.838(3) Å) is identical within the margin of error to the Si–C distances involving the T_8 -phenyl substituents and indistinguishable from those reported for T_8Ph_8 ^[27] (1.838(2) to 1.843(2) Å) as well as an octa(*p*-carboxyphenylethyl)- T_8 (1.840(4) to 1.851(4) Å).^[28] The SiO bond lengths of the T_8 cage are between 1.606(2) Å and 1.627(2) Å, thus showing slightly more variance compared to T_8Ph_8 (1.6166(11) to 1.6258(11) Å). As a consequence of the reduced symmetry, the T_8 silicon atoms of **5** deviate slightly more from the ideal tetrahedral coordination with angles between 103.9(3) and 116.3(3)°. In comparison, the silicon atoms of T_8Ph_8 exhibit bond angles from 107.72(6) to 111.58(6)°. The same applies to the angles at the oxygen cage atoms with values between 137.6(1)° and 168.0(2)° compared to T_8Ph_8 (min. 142.28(7) and max. 153.22(8)°). The ethylene signals undergo downfield shifts to 2.98–2.91 ppm and 1.41–1.34 ppm (previously 2.79–2.75 ppm and 1.16–1.12 ppm) in the ¹H NMR and 28.93 and 15.34 ppm in the ¹³C NMR respectively (**4**: 28.83 and 14.14 ppm).

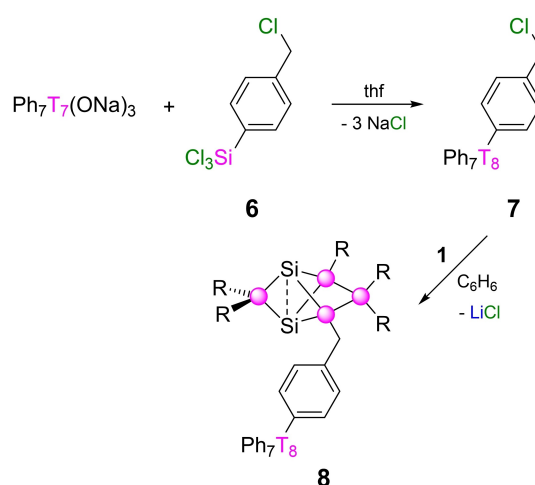
As to be expected for the substitution of the electron-withdrawing chloro group, the ¹H NMR signal of the benzylic proton in **5** is no longer observed at 4.08 ppm but most likely obscured by the Tip groups of the hexasilabenzpolarene through an upfield shift. The benzylic carbon atom of **5** is observed at 20.34 ppm (**4**: 46.19 ppm). The ²⁹Si NMR shows diagnostic signals for an intact hexasilabenzpolarene motif^[19a,b] at 170.6 ppm for the *privo*-position, 14.1, 8.4 and 1.0 ppm for the two *ligato*- and the *remoto*-vertices as well as –261.1 and –275.9 ppm for the two *nudo*-positions. The silsesquioxane signals observed at –65.3, –77.6 and –77.9 ppm are comparable to the precursor **4** (–65.4, –77.6 and –78.0 ppm). The ²⁹Si CP/MAS NMR spectrum shows almost identical signals to those

in solution, indicating a very similar structure in the solid state (Experimental Section/SI).

The longest wavelength absorption in the UV/Vis spectrum of **5** at 470 nm ($\epsilon = 540 \text{ M}^{-1} \text{ cm}^{-1}$) is marginally blue-shifted compared to the all-Tip substituted hexasilabenzpolarene **E** (473 nm).^[18d]

With compound **5** as proof-of-principle in hand, we attempted the installation of a shorter linking unit between the siliconoid and silsesquioxane motifs, that is without the ethylene bridge between the T_8 cage and the *para*-phenylene spacer. Corner capping the incompletely condensed silsesquioxane $Ph_7T_7(O_4Na)_3$ through a modified literature procedure^[29] with commercially available 4-(chloromethyl)phenyltrichlorosilane **6** gives **7** in 11% isolated yield. Subsequent treatment of **7** with the anionic siliconoid **1** indeed results in **8**, which was isolated in 74% crystalline yield by slowly cooling down a 75 °C hot benzene solution during 15 h (Scheme 3).

Unfortunately, no single crystals of **8** could be obtained so that the comparison of physical data with those of **5** is limited to the NMR spectroscopic investigations. As in **5**, the hexasilabenzpolarene motif of **8** shows the typical distribution of ²⁹Si NMR signals.^[18d;19a,b] The shortened linking unit has close to no discernible effect on the chemical shifts. The absence of the ethylene bridge at the silsesquioxane side of the linker is reflected in the ²⁹Si NMR spectrum of **8**. All corners of the T_8 unit are directly substituted by aryl groups giving rise to four signals (instead of three in **5**), which are closely grouped together at chemical shifts of –76.8, –77.5, –77.6 and –77.7 ppm. A total correlation spectroscopy (TOCSY) experiment was used to verify the linkage of the cluster compounds spectroscopically. Cross signals in the TOCSY experiment indicate the successful connection of the silsesquioxane (see Supporting Info). Compound **8** also exhibits a longest wavelength absorption of 470 nm ($\epsilon = 540 \text{ M}^{-1} \text{ cm}^{-1}$).



Scheme 3. Corner-capping reaction using trichlorosilane with shorter linking group **6** to yield monofunctionalized T_8 as well as subsequent reaction with *ligato*-lithiated hexasilabenzpolarene to yield the potential SiO model system **8** (R = Tip = 2,4,6-triisopropylphenyl).

Conclusions

Suitably functionalized T_8 -silsesquioxanes react with a lithiated hexasilabenzpolarene to yield interconnected molecular species featuring both uncompromised silicon-rich and oxygen-rich moieties, the siliconoid and the T_8 silsesquioxane, respectively. With the overall Si:O ratio of 14:12 these molecules approximately reflect the stoichiometry of silicon monoxide and thus represent potential molecular model systems. With the non-conjugated linkers employed here, however, only very small structural and spectroscopic effects result. One of the inter-linked species was fully characterized by single-crystal X-ray diffraction leaving no doubt regarding the constitution of the other based on the similarity of spectroscopic data. The synthesis of derivatives with fully π -conjugated linking units and possibly more realistic σ -conjugated oligosilane linkers is currently being investigated in our laboratory.

Experimental Section

General. All manipulations were conducted under a protective argon atmosphere using standard Schlenk techniques or a glovebox. Non-chlorinated solvents were dried over Na/benzophenone (in the presence of tetraglyme in case of aromatic and aliphatic solvents) and distilled under argon atmosphere. Deuterated solvents were dried by reflux over potassium and distilled under argon atmosphere prior to use. Chlorinated deuterated solvents were refluxed and distilled over P_4O_{10} and stored under Argon atmosphere. NMR spectra were recorded on either a Bruker Avance III 300 NMR spectrometer (1H : 300.13 MHz, ^{13}C : 75.46 MHz, ^{29}Si : 59.63 MHz) or a Bruker Avance III 400 spectrometer (1H : 400.12 MHz, ^{13}C : 100.61 MHz, ^{29}Si : 79.49 MHz) at 300 K. UV/VIS spectra were recorded on a Shimadzu UV-2600 spectrometer in quartz cells with a path length of 0.1 cm. Melting points were measured in sealed NMR caps under Ar atmosphere. Elemental analysis was carried out with an elemental analyzer Leco CHN-900. $T_7Ph_7(OH)_3$ was obtained from Hybrid Plastics and dried under vacuum prior to use. 4-vinylbenzyl chloride was obtained from Sigma Aldrich and degassed before use. Platinum on activated carbon was obtained from abcr. Trichlorosilane was obtained from abcr and distilled prior to use. Sodium hydride was obtained from Sigma Aldrich, washed with hexane and stored under argon atmosphere. Triethylamine was obtained from Merck, stirred over calcium hydride overnight and distilled prior to use. Calcium hydride was obtained from Acros Organics and used as received. (2,2,5,5,6-Pentakis(2',4',6'-triisopropylphenyl)tetracyclo[2.2.0.0^{1,3}.0^{3,6}]hexasilan-4-yl)lithium **1** was synthesized according to the published procedure.^[19a]

Deprotonation of heptaphenylsilsesquioxanetriol with sodium hydride. The synthesis was carried out according to a modified literature procedure.^[30] A solution of 21.17 g (22.70 mmol) of $T_7Ph_7(OH)_3$ in 80 mL thf was added dropwise to a suspension of 1.69 g (70.4 mmol) sodium hydride in 30 mL thf at room temperature in three hours. The reaction mixture was stirred for 24 hours, after which the solvent was evaporated. 23.20 g (90%) of a white solid were obtained. 1H NMR (400 MHz, $CDCl_3$, 300 K): 8.08–5.87 (m, 35 H, Ar-H), 3.40 (m, 8 H, thf), 1.54 (m, 8 H, thf) ppm.

Preparation of the benzyl-functionalized siliconoid **2.** The *ligato*-lithiated hexasilabenzpolarene **1** (200 mg; 0.127 mmol) is dissolved in 2 mL benzene and 1.1 eq benzylbromide (23.96 mg; 16.64 μ L; 0.14 mmol) are added at room temperature under stirring. After stirring the dark orange solution for 15 h, the precipitation of LiBr as white solid can be observed. Benzene is distilled off in vacuum

at room temperature. The orange residue is digested with 4 mL hexane and extracted with hexane at room temperature. After evaporation of hexane in vacuum, the crude product is dissolved in 0.5 mL pentane to afford 122 mg (75%) of **2** as orange crystals. 1H -NMR (300.13 MHz, C_6D_6 , 300 K): 7.62, 7.24 ($C_{10}H_8$), 7.13–6.69 (br, 9 H, Ar-H), 5.91–4.37 (br, 1 H, Tip-H), 4.37–3.91 (br, 2 H, Tip- ^{i}Pr -CHMe₂), 2.85–2.57, 2.47–2.36 (each br, together 4 H, Tip- ^{i}Pr -CHMe₂), 2.21–0.02 (br, overlapping with thf, all together 72 H, Tip- ^{i}Pr -CH₃) ppm. ^{29}Si -NMR (59.62 MHz, C_6D_6 , 300 K): 170.6 (Tip₂-Si), 14.0 (Tip-Si), 8.5 (Tip₂-Si), 1.3 (s, Si-C-Ph), –260.9, –276.0 (each br, Si-Si₃) ppm.

4-(Chloromethyl)phenethyltrichlorosilane **3.** The synthesis was carried out according to a modified literature procedure.^[24] A mixture of 0.19 g platinum on activated carbon, 200 mL toluene, 13.50 mL (95.80 mmol) of 4-vinylbenzyl chloride and 14.50 mL (143.45 mmol) of trichlorosilane was refluxed at 80 °C for 4 hours, stirring was continued at room temperature for another 17 h. The mixture was filtered over Celite 545 and all volatiles were distilled off at 10^{–2} mbar. Distillation at 10^{–5} mbar using an oil diffusion pump and 120 °C afforded 18.55 g (67%) of **3** as a deep yellow liquid. 1H NMR (400 MHz, $CDCl_3$, 300 K): 7.36–7.22 (m, 4 H, Ar-H), 4.59 (s, 2 H, Ar-CH₂-Cl), 2.93–2.89 (m, 2 H, Ar-CH₂-CH₂), 1.78–1.73 (m, 2 H, Si-CH₂-CH₂) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 141.81, 135.87, 129.09, 128.42 (each Ar-C), 46.13 (Ar-CH₂-Cl), 28.08 (Ar-CH₂-CH₂), 26.08 (Si-CH₂-CH₂) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 300 K): 11.8 ppm.

Corner-capping reaction of $Ph_7T_7(OH)_3$ with 4-(chloromethyl)phenethyltrichlorosilane. Preparation of **4 (T_8Ph_7R ; R=4-(chloromethyl)phenethyl).** This synthesis was carried out according to a modified literature procedure.^[23] A suspension of 14.68 g (14.72 mmol) of $T_7(OH)_3$ and 6.60 mL (47 mmol) NEt_3 in 250 mL dry thf was stirred for 30 minutes and then cooled down in an ice-water bath for 1 h. A solution of 3.85 mL (17.66 mmol) of 4-(chloromethyl)phenethyltrichlorosilane **3** in 150 mL of dry thf was added dropwise during 3.5 h and stirring continued for 14 h in the thawing ice-bath. The solvent was evaporated, and the white residue dissolved in 150 mL of chloroform. The organic phase was washed three times with water and dried over magnesium sulfate. The product was precipitated by pouring the organic phase into 100 mL of MeOH. Drying in vacuum yielded 7.47 g (6.73 mmol, 46%) of **4** as a white solid (m.p. > 300 °C). 1H NMR (400 MHz, C_6D_6 , 300 K): 7.89–7.81 (m, 14 H, T_8 -*m*-Ar-H), 7.15–7.00 (m, 21 H, T_8 -*o,p*-Ar-H), 6.93–6.83 (m, 4 H, *o,m*-Ar-H), 4.08 (s, 2 H, Ar-CH₂-Cl), 2.79–2.75 (m, 2 H, Ar-CH₂-CH₂), 1.16–1.12 (m, 2 H, T_8 -CH₂-CH₂) ppm. ^{13}C NMR (100 MHz, C_6D_6 , 300 K): 144.12, 135.28, 134.64, 134.60, 131.27, 131.24, 130.69, 130.45, 130.39, 128.89, 128.43, 128.36, 128.20, 127.94 (each Ar-C), 46.19 (Ar-CH₂-Cl), 28.83 (Ar-CH₂-CH₂), 14.14 (T_8 -CH₂-CH₂) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6 , 300 K): –65.4 (O_3Si -CH₂), –77.6 (O_3Si -Ph), –78.0 (O_3Si -Ph) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 300 K): –65.8 (O_3Si -CH₂), –78.3 (O_3Si -Ph), –78.6 (O_3Si -Ph) ppm.

Preparation of hybrid system **5.** A solution of the *ligato*-lithiated hexasilabenzpolarene **1** in C_6H_6 (7.5 mL) was added dropwise to 388 mg (0.35 mmol) of the linker-substituted silsesquioxane **4** in 5 mL benzene during 25 minutes. The mixture was stirred at room temperature for another 45 minutes and filtered. The solvent was reduced to half of its volume and 213 mg (31%) of orange crystals of **5** were grown by heating the solution to 75 °C in an oil bath and letting it cool down slowly to rt overnight. Single crystals suitable for an X-ray diffraction study were grown by adding hexane to the amorphous solid to form a suspension. Dropwise addition of toluene while heating gently dissolved all solids and standing for three days at room temperature produced orange needles of **5** as single crystals. (m.p. 200–201 °C, no dec.). 1H NMR (400 MHz, C_6D_6 , 300 K): 7.97–7.79 (m, 14 H, T_8 -*m*-Ar-H), 7.63, 7.25 ($C_{10}H_8$), 7.19–7.00 (m, 27 H, overlapping T_8 -*o,p*-Ar-H with Tip-CH), 6.97 (br, 2 H, Tip-CH), 6.95–6.82 (m, 4 H, *o,m*-Ar-H), 6.80 (br, 1 H, Tip-CH), 5.11, 4.57

(each br, 1 H, ⁱPr-CH), 4.24 (br, 2 H, ⁱPr-CH), 4.17–3.99 (m, overlapping, 2 H, ⁱPr-CH), 3.44, 3.31, 3.12 (each br, 1 H, ⁱPr-CH), 2.98–2.91 (m, 2 H, Ar-CH₂-CH₂), 2.69, 2.68 (each sept., overlapping, 4 H, ⁱPr-CH), 2.39 (sept., ³J_{H,H} = 6.90 Hz, 1 H, ⁱPr-CH), 2.17 (br, 3 H, ⁱPr-CH₃), 1.93 (br, 1 H, ⁱPr-CH), 1.75, 1.63 (each br, 6 H, ⁱPr-CH₃), 1.60–1.42 (m, 19 H, ⁱPr-CH₃), 1.41–1.34 (m, 2 H, Si-CH₂-CH₂), 1.33–1.01 (m, overlapping, 32 H, ⁱPr-CH₃), 0.85–0.68 (br, overlapping, 20 H, ⁱPr-CH₃), 0.65, 0.36, 0.23 (each br, 3 H, ⁱPr-CH₃) ppm. ¹³C NMR (100 MHz, C₆D₆, 300 K): 157.30, 155.13, 154.11, 153.50, 152.70, 150.82, 150.78, 150.63, 149.36, 140.88, 137.78, 136.73, 134.70, 134.67, 134.64, 131.26, 131.21, 130.76, 130.50, 130.45, 130.05, 127.40, 126.07, 124.02, 123.52, 123.42, 123.05, 122.46, 122.07, 121.45, (each Ar-C), 37.77, 36.56, 36.11, 34.74, 34.42, 34.38, 31.97, (each Tip-ⁱPr-CH and Tip-ⁱPr-CH₃), 28.93 (Ar-C, 27.50, 27.14, 26.51, 25.61, 24.48, 24.18, 24.06, 23.86, 23.47, 23.07, 22.55 (each Tip-ⁱPr-CH and Tip-ⁱPr-CH₃), 20.33 (Ar-CH₂-Si), 15.34 (Si-CH₂-CH₂), 14.39 ppm. ²⁹Si NMR (79.5 MHz, C₆D₆, 300 K): 170.6 (Tip₂Si), 14.1 (Tip-Si), 8.4 (Tip₂-Si), 1.0 (Si-C-Ar), -65.3 (O₃Si-CH₂), -77.6, -77.9 (each O₃Si-Ph), -261.1, -275.9 (each Si-Si₃) ppm. CP-MAS ²⁹Si NMR: (79.5 MHz, 11 kHz, C₆D₆, 300 K): 168.3 (Tip₂Si), 18.1, 5.0, 1.9 (RSi₃Si), -67.4 (O₃Si-CH₂), -79.0 (O₃Si-Ph), -264.8, -274.3 (each Si-Si₃) ppm. UV/VIS (n-hexane): λ_{max}(ε) = 470 nm (540 M⁻¹ cm⁻¹), 375 nm (8190 M⁻¹ cm⁻¹). Elemental Analysis: Calc. for C₁₂₆H₁₆₀O₁₂Si₁₄: C, 66.96; H, 7.15; Found: C, 67.03; H, 7.43.

Corner-capping reaction of T₇Ph₇(ONa)₃ with 4-(chloromethyl)phenyl-trichlorosilane. Preparation of 7 (T₈Ph₇R; R=4-(chloromethyl)phenyl). This synthesis was carried out according to a modified literature procedure.^[29] A suspension of 26.50 g (26.57 mmol) of T₇(ONa)₃ and 12.5 mL (89.70 mmol) NEt₃ in 300 mL thf was stirred for 20 minutes and cooled in an ice-water bath for one hour. 4-(Chloromethyl)phenyltrichlorosilane 6 in 125 mL of thf was added dropwise during 2 h in the cold. The reaction mixture was allowed to reach room temperature and stirring continued for another 15 hours. All volatiles were removed under vacuum and 500 mL of CH₂Cl₂ were added. The mixture was filtered and the solvent reduced until precipitation started to occur. The residue was collected and washed with 100 mL dichloromethane. The product 7 (3.15 g; 2.92 mmol) was collected as a white solid in 11 % yield (m.p. > 300 °C). ¹H NMR (400 MHz, C₆D₆, 300 K): 7.86–7.84 (m, 14 H, T₈-m-Ar-H), 7.74–7.72 (m, 2 H, Ar-o,m-H), 7.11–7.01 (m, 21 H, T₈-o,p-H), 6.90–6.88 (m, 2 H, Ar-o,m-H), 3.92 (s, 2 H, Ar-CH₂) ppm. ¹H NMR (400 MHz, CD₂Cl₂, 300 K): 7.80–7.78 (m, 14 H, T₈-m-Ar-H), 7.50–7.39 (m, 26 H, Ar-o,m-H overlapping with T₈-o,p-H), 4.60 (s, 2 H, Ar-CH₂) ppm. ¹³C NMR (100 MHz, CD₂Cl₂, 300 K): 140.66, 134.88, 134.41, 131.33, 130.79, 130.45, 130.41, 128.50, 128.40 (each Ar-C), 46.42 (Ar-CH₂-Cl) ppm. ²⁹Si NMR (79.5 MHz, CD₂Cl₂, 300 K): -78.31, -78.35, -78.6 ppm.

Preparation of hybrid system 8. A mixture of 273 mg (0.253 mmol) of silsesquioxane 7 and 372 mg (0.256 mmol) of the *ligato*-lithiated hexasilabenzpolararene 1 in benzene (5 mL) was stirred at room temperature for 75 min. The resulting dark orange mixture was filtered by cannula and the filtrate reduced in vacuum until a viscous solution was obtained. Orange crystals of 8 (417 mg, 74 %) were obtained by heating the benzene solution to 75 °C in an oil bath and letting it cool down slowly during 14 h (m.p. 200–201 °C, no dec.). ¹H NMR (400 MHz, C₆D₆, 300 K): 8.04–7.97 (m, 7 H, Ar-H), 7.89–7.77 (m, 14 H, Ar-H), 7.29–7.21 (m, 13 H, Ar-H), 7.13–7.01 (m, 20 H, Ar-H), 7.00–6.88 (m, 10 H, Ar-H and Tip-CH), 6.85 (br, 2 H, Tip-CH), 6.79 (br, 1 H, Tip-CH), 5.10 (br, 1 H, ⁱPr-CH), 4.56 (br, 1 H, ⁱPr-CH), 4.23 (br, 1 H, ⁱPr-CH), 4.08 (br, 4 H, overlapping, ⁱPr-CH), 3.41, 3.29, 3.10 (each br, 1 H, ⁱPr-CH), 2.76–2.59 (m, 5 H, overlapping, ⁱPr-CH), 2.28 (sept, 1 H, ⁱPr-CH), 2.16 (br, 3 H, ⁱPr-CH), 1.76–1.04 (m, 79 H, overlapping, ⁱPr-CH₃), 0.80 (br, 5 H, ⁱPr-CH₃), 0.72 (br, 8 H, overlapping, ⁱPr-CH₃), 0.62 (br, 17 H, overlapping, ⁱPr-CH₃), 0.35, 0.22 (each br, 4 H, ⁱPr-CH₃) ppm. ¹³C NMR (100 MHz, C₆D₆, 300 K): 156.90,

154.70, 153.65, 153.01, 152.29, 150.68, 150.50, 150.32, 148.92, 148.77, 144.11, 137.83, 136.17, 135.44, 134.46, 134.36, 134.30, 133.74, 133.69, 130.87, 130.82, 130.49, 130.12, 129.47, 128.23, 128.01, 127.94, 127.89, 127.82, 127.70, 127.58, 127.46, 125.71, 123.62, 123.07, 122.66, 122.07, 121.72, 121.10, (each Ar-C) 37.44, 36.28, 36.05, 35.78, 35.39, 34.86, 34.46, 34.37, 34.01, 33.95, 28.36, 27.59, 26.99, 26.75, 26.10, 25.33, 24.28, 24.12, 23.82, 23.68, 23.50, 22.98, 22.71, 22.23, (each Tip-ⁱPr-CH and Tip-ⁱPr-CH₃), 20.94 (Ar-CH₂-Si) ppm. ²⁹Si NMR (79.5 MHz, C₆D₆, 300 K): 170.8 (Tip₂Si), 14.3 (Tip-Si), 8.8 (Tip₂-Si), 1.9 (Si-C-Ar), -76.8, -77.5, -77.6, -77.7 (each O₃Si-Ar), -260.5, -276.2 (each Si-Si₃) ppm. CP-MAS ²⁹Si NMR: (79.5 MHz, 11 kHz, 300 K): 167.1 (Tip₂Si), 9.1, 5.0 (each RSi₃Si), -78.9 (O₃Si-Ar), -255.0, -281.7 (each Si₃Si) ppm. UV/VIS (n-hexane): λ_{max}(ε) = 470 nm (540 M⁻¹ cm⁻¹), 362 nm (8510 M⁻¹ cm⁻¹). Elemental Analysis: Calc. for C₁₂₄H₁₅₆O₁₂Si₁₄: C, 66.73; H, 7.05; Found: C, 68.86; H, 5.98.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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