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Spherical, Polyfunctional Molecules Using Poly(bromophenylsilsesquioxane)s as Nanoconstruction Sites

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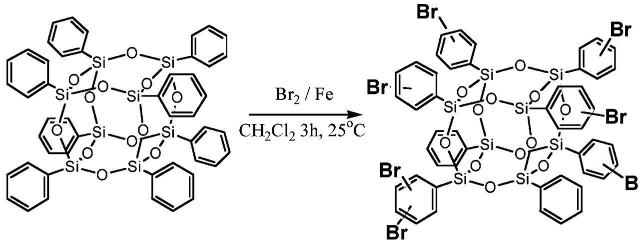
ABSTRACT: Poly(bromooctaphenylsilsesquioxane)s (Br_xOPS) are easily synthesized from octaphenylsilsesquioxane (OPS) via bromination with Br_2/Fe in dichloromethane. For Br:OPS ratios less than 8:1, singly brominated products are obtained with 65−70% para substitution, 25−20% meta substitution and the remainder ortho. Higher ratios provide dibrominated products up to $Br_{16}OPS$. Surprisingly, the disubstitution pattern is completely different with 80% 2,5 substitution (meta and ortho to Si), indicating extensive rearrangement with addition of the second bromine. Br_xOPS bromo functionality is readily transformed via low temperature catalytic coupling reactions with para-substituted styrenes, tetraphenylborate, methyl methacrylate, or toluidine into the corresponding fully substituted *p*-stilbenes, *p*-biphenyls, methyl cinnamates, and diarylamines. The *p*-stilbenes offer unusually large red shifts and order of magnitude increases on photoluminescence quantum efficiencies over stilbene itself. Methyl methacrylate addition provides a mechanism for forming cross-linkable films and can be used in conjunction with the other functionalization reactions. Reactions with phenylacetylenes occur with concomitant formation of vinyl bromides, which appear to react further, adding second acetylene groups. The fact that each phenyl group occupies a different octant in Cartesian space, for $Br_{\leq 8}OPS$ primarily para, offers the opportunity to create novel eight branched, highly conjugated cores of value in their own right but also of value as three-dimensional, eight or 16 branched, aromatic cores for the synthesis of dendrimer-like and/or hyperbranched molecules.

Introduction

Cubic silsesquioxanes, $[RSiO_{1.5}]_8$, are unique molecules.[1−15] They consist of rigid, single-crystal silica cores with eight vertices (opposing vertex body diagonal = 0.53 nm) to which are appended organic functional groups creating organic/inorganic spherelike molecules 1−2 nm in diameter with volumes <2 nm^3. Each group lies in a separate octant in Cartesian space. The positioning of the functional groups, the variety of groups possible, and their nanometer size provide many opportunities for using cubes to build nanocomposite/hybrid materials in one, two, or three dimensions, one nanometer at a time. Moreover, the core adds the rigidity and heat capacity of SiO_2 making these compounds exceptionally robust.

Cubes and related polyhedral silsesquioxanes have been successfully used to model catalytic surfaces,[1] develop new catalysts[2] and novel porous media,[3] serve as NMR standards,[4] act as novel encapsulants,[5] and act as building blocks for nanocomposite materials.[6−10] We recently described the synthesis of octa(aminophenyl)silsesquioxane (OAPS, *m*:*o*-65:25) from octaphenylsilsesquioxane[11,12] (OPS) and its utility in synthesizing novel nanocomposites with excellent control of 3-D periodicity, and sets of related compounds of potential use as nanoconstruction sites/nanobuilding blocks.[13−16] We report here that bromination of OPS (Scheme 1), done easily at 100 g scales, provides different and equally useful nanobuilding blocks, Br_xOPS, where x = average number of bromines/OPS.[16] We further describe the use of catalytic coupling reactions that permit the complete replacement of these bromines with a variety of functional groups at low temperatures.

Scheme 1. Synthesis of Brominated Octaphenylsilsesquioxanes (Br_xOPS) Where "x" Represents the Average Number of Bromines Per Molecule



Experimental Section

Materials. Methylene chloride was purchased from Fisher and distilled from CaH_2 prior to use. Dioxane, toluene, and THF were purchased from Fisher and distilled from Na/benzophenone. Octaphenylsilsesquioxane was produced by previously published methods.[12] Bis(tri-*tert*-butylphosphine)palladium(0) was purchased from Strem and used as received. All other chemicals were purchased from Fisher or Aldrich and used as received.

NMR Analyses. All ^1H and ^{13}C NMR spectra were performed in $CDCl_3$ and recorded on a Varian INOVA 400 MHz

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spectrometer. ^{1}H NMR spectra were collected at 400.0 MHz using a 6000 Hz spectral width, a relaxation delay of 3.5 s, 30K data points, a pulse width of 38°, and $CHCl_3$ (7.27 ppm) as the internal reference. For bromination experiments, a known volume of THF was added as an internal standard.

Thermogravimetric Analyses. All TGA analyses were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer (Perkin-Elmer Co., Norwalk, CT), under dry air with a flow rate of 60 mL/min and a heating rate of 10C°/min. Alumel and iron supplied by the manufacturer were used to calibrate the system. Samples were dried under vacuum for a minimum of 3 h prior to analysis, and heated to 120 C° for 10 min inside the TGA before analysis to remove adsorbed water.

Gel Permeation Chromatography. All GPC analyses were performed on a Waters 440 system equipped with Waters Styragel columns (7.8 × 300, HT 0.5, 2, 3, 4) with RI detection using an Optilab DSP interferometric refractometer and THF as solvent. The system was calibrated using polystyrene standards and toluene as reference.

Matrix-Assisted Laser-Desorption/Time-of-Flight Spectrometry. MALDI−TOF was performed on a Micromass TofSpec-2E equipped with a 337 nm nitrogen laser in positive-ion reflection mode using poly(ethylene glycol) as the calibration standard, dithranol as the matrix, and $AgNO_3$ as the ion source. Samples were prepared by mixing solutions of five parts dithranol (10 mg/mL in THF), five parts sample (1 mg/mL in THF) and one part $AgNO_3$ (10 mg/mL in water) and blotting the mixture on the target plate.

Synthesis of Br_xOPS, $x = 5.3$. To a 250 mL round-bottom flask equipped with magnetic stirring was added 5.0 g of finely ground OPS (38.7 mmol-phenyl), 570 mg (10.2 mmol) of Fe, and 50 mL of CH_2Cl_2. Then, 1.78 mL (34.8 mmol) of Br_2 was added over the course of 10 min via syringe. The solution was stirred at ambient for 3 h. After this time, 50 mL of 10% $NaHSO_3$ was added to destroy the remaining Br_2. The organic layer was separated and washed with water three times, and the solvent was removed by rotoevaporation. The resulting white powder was dissolved in 50 mL of ethyl acetate and precipitated into 1000 mL of methanol. The solution was filtered, giving 6.1 g (87%) of a white powder.

Characterization Data. MALDI−TOF: *m/z* = 1376.4, 1456.3, 1534.2, 1614.1, 1692.0, 1771.9, 1849.8 ($AgBr_6Si_8O_{12}C_{48}H_{34}$ = 1614 amu). ^{1}H NMR: 6.8−8.1 ppm (br). ^{13}C NMR ($CDCl_3$): 137.1, 136.0, 134.4, 133.1, 132.9, 131.6, 130.2, 128.5, 126.7, 124.6, 123.7 ppm. ^{29}Si NMR (TMS): −77.87, −79.39, −81.83 ppm. TGA: found, 33.1%; calcd, 34.7%. $T_{d5\%}$ = 424 °C. GPC: M_n = 921; M_w = 928; PDI = 1.01. GC−MS (post TBAF cleavage): 95% bromobenzene; 5% dibromobenzene (benzene cannot be quantified by this method).

(i) Synthesis of *p*-Methylstilbene Derivative from Br_xOPS ($x = 5.3$). To a dry 50 mL Schlenk flask under N_2 was added 0.500 g of $Br_{5.3}$OPS (1.83 mmol −Br), bis(tri-*tert*-butylphosphine)palladium(0) (0.056 mmol, 24 mg) and tris(dibenzylidenacetone)dipalladium (0, $Pd_2(dba)_3$) (0.028 mmol, 22 mg). 1,4-dioxane (10 mL) was then added by syringe, followed by dicyclohexylmethylamine (NCy_2Me, 3.12 mmol, 0.56 mL) and 4-methylstyrene (0.949 mL, 7.3 mmol). The mixture was stirred at room temperature for 48 h and then quenched by filtering through 1 cm of Celite, which was washed with 5 mL of THF. The solution was then precipitated into 150 mL of methanol, filtered and the solid redissolved in 10 mL of THF. This solution was then filtered again through a 1 cm Celite column to remove any remaining Pd particles, and reprecipitated into 150 mL of methanol. The resulting powder was filtered and dried in vacuo for 3 h, yielding 0.441 g (78%) of a white powder.

Characterization Data. MALDI−TOF: *m/z* (Ag$^+$ adduct) = 1374.9, 1491.0, 1607.2, 1723.3, 1839.4, 1955.5, 2071.2 [$AgSi_8O_{12}C_{48}H_{34}(C_9H_9)_6$ = 1838 amu]. ^{1}H NMR ($CDCl_3$): 6.7−8.1 ppm (br, 14H), 2.34 ppm (m, 3H).^{13}C NMR ($CDCl_3$): 25.2, 126.2, 126.7, 126.9, 127.8, 128.2, 128.8, 128.9, 134.5, 134.8, 137.4 ppm. TGA (air, 1000 °C): found, 29.2%; calcd, 27.8%. $T_{d5\%}$ = 410 °C. GPC: M_n = 1669; M_w = 1786; PDI = 1.07. GC−MS (post (TBA)F cleavage): 96% *trans*-*p*-methylstilbene; 4% *cis*-*p*-methylstilbene; 0% distyrylbenzenes.

(ii) Synthesis of *p*-Methyldiphenylacetylene Derivatives from Br_xOPS ($x = 5.3$). To a dry 50 mL Schlenk flask under N_2 and equipped with a magnetic stir bar was added 0.500 g of $Br_{5.3}$OPS (1.83 mmol Br), CuI (18.2 mg, 0.096 mmol), $Pd_2(dba)_3$ (22.08 mg, 0.048 mmol), bis(tri-*tert*-butylphosphine)-palladium(0) (24.5 mg, 0.096 mmol), 5.0 mL 1,4 dioxane (previously distilled under N_2), 0.36 mL (2.6 mmol) of triethylamine, and *p*-methylphenylacetylene (0.66 mL, 6.0 mmol). The solution was stirred at 25 °C for 48 h, during which time it turned dark gray-brown. The mixture was poured into excess methanol to deactivate the catalyst. Volatiles were removed by rotary evaporation. The residue was dissolved in 5.0 mL of ethyl acetate, filtered through Celite, and precipitated into 100 mL of methanol. The light orange powder was collected by filtration and dried in vacuo for 5 h, giving 0.454 g (85%).

Characterization Data. MALDI−TOF: (Ag$^+$ adduct) *m/z* = 1606.7, 1640.8, 1684.6, 1720.7, 1754.8, 1798.6, 1834.7, 1868.8, 1912.6, 1948.7, 1984.7, 2027.7 [$AgSi_8O_{12}C_{48}H_{34}(C_9H_7)_4Br_2$ = 1755 amu] (51% of Br reacted to form 4-methyldiphenylacetylene based on retained Br, see discussion). ^{1}H NMR ($CDCl_3$): 7.0−7.9 (br, m, 6.4H), 6.5 (s ≈ 0.3H), 2.33 (s, 1.33H), 2.15 (s, 1.7H) ppm. ^{13}C NMR ($CDCl_3$): 14.5, 136.0, 134.1, 131.7, 129.3, 123.2, 111.9 ppm. TGA (air, 1000 °C): found, 30.3%; calcd, 31.1%. $T_{d5\%}$ = 480 °C. GPC: M_n = 1118; M_w = 1194; PDI = 1.07.

(iii) Synthesis of Biphenyl Derivatives via Tetra(aryl) Borates from Br_xOPS ($x = 5.3$).[5] To a dry 25 mL Schlenk flask under N_2 was added 1 g of $Br_{5.3}$OPS (3.65 mmol of Br), tetrakis(triphenylphosphine)palladium(0) (90 mg, 0.08 mmol) and sodium tetraphenylborate (1.377 g, 4.04 mmol). 1,4-Dioxane (5 mL) was then added by syringe. The suspension was stirred vigorously at 50° C for 18 h and then quenched by washing twice with 75 mL of ethyl acetate and 75 mL of water. The aqueous layer was discarded, and the organic layer was filtered through Celite, dried with sodium sulfate, and then concentrated by rotary evaporation. The resulting concentrate was diluted with THF to 10 mL and then precipitated in 50 mL of ethanol to afford a light brown powder. The resulting powder was filtered and dried in vacuo for 3 h.

Characterization Data. MALDI−TOF: *m/z* (Ag$^+$ adduct) = 1369.1, 1445.2, 1521.2, 1597.3, 1673.3, 1750.4, 1826.5, 1902.5 [$AgSi_8O_{12}C_{48}H_{34}(C_6H_5)_6$ = 1597 amu]. TGA: found, 32.6%; calcd 33.5%. $T_{d5\%}$ = 470 °C. GPC: M_n = 1983; M_w = 2027; PDI = 1.02. GC−MS (post (TBA)F cleavage): 99% bipheny; 1% bromobenzene.

(iv) Synthesis of Methacrylate Derivative from Br_xOPS ($x = 5.3$).[2] To a dry 50 mL Schlenk flask under N_2 was added 0.500 g $Br_{5.3}$OPS (1.83 mmol Br), bis(tri-*tert*-butylphosphine) palladium(0) (0.056 mmol, 24 mg) and tris(dibenzylidenacetone)dipalladium(0) (0.028 mmol, 22 mg). 1,4-Dioxane (10 mL) was then syringed in, followed by dicyclohexylmethylamine (3.12 mmol, 0.56 mL), and 7.3 mmol of methyl methacrylate. The mixture was stirred at ambient for 48 h and then quenched by filtering through 1 cm of Celite, which was then washed with 5 mL of THF. The solution was then precipitated into 150 mL of methanol and filtered, and the solid was redissolved in 10 mL of THF. This solution was again filtered through a 1 cm Celite column to remove any remaining Pd particles, and reprecipitated into 150 mL of methanol. The resulting powder was filtered and dried in vacuo for 3 h, giving 0.317 g (58%) of an off-white powder.

Characterization Data. MALDI−TOF: *m/z* (Ag$^+$ adduct) = 1534.0, 1629.8, 1728.8, 1826.9, 1925.0, 2022.8 [$AgSi_8O_{12}C_{48}H_{34}(C_5H_7O_2)_6$ = 1729 amu]. ^{1}H NMR ($CDCl_3$): 7.3−7.8 (br, 8H), 3.5−3.9 (m, 3H) 1.8−2.1 ppm (m, 3H). TGA (air, 1000 °C): found, 28.3%; calcd, 30.8%. $T_{d5\%}$ = 270 °C. GPC: M_n = 2450; M_w = 3015; PDI = 1.23.

(v) Amine Coupling with *m*-Toluidine.[6] Tris(dibenzylidenacetone)dipalladium(0) (0.046 g, 0.05 mmol), and 1,1′-bis(diphenylphosphino)ferrocene (0.041 g, 0.075 mmol) were placed in 100 mL flask equipped with a condenser and dissolved in 25 mL of dry toluene and stirred at ambient for 15 min under N_2. $Br_{5.3}$OPS (0.5 g, 1.83 mmol Br) was then added, followed by *m*-toluidine (2.57 mL, 2.4 mmol) and NaO^{t}Bu (0.277 g, 2.9 mmol). After being stirred at 100 °C for

3 h, the mixture was cooled to ambient, 100 mL of 5% HCl was added and the organic layer extracted with 50 mL of toluene. The organic layer was dried over Na_2SO_4. The crude product obtained after removing solvent at reduced pressure, was precipitated into hexane, redissolved in toluene, and reprecipitated into hexane. The yield was 0.374 g (75%) of an off-white powder.

Characterization Data. MALDI−TOF *m/z*: (Ag^+ adduct) = 1507, 1534, 1612, 1639, 1692, 1718, 1744, 1798, 1824, 1851, 1876, 1904, 1926, [$AgSi_8O_{12}C_{48}H_{34}$ $(C_7H_8N)_4Br_2$ = 1718 amu] (63% of Br reacted to form diphenyl(methyl)amino). ^1H NMR ($CDCl_3$): 6.8−8.0 (br, m, 15 H), 5.7 (s, 0.5H), 5.6 (s, 0.2H), 2.3 (s, 2.5 H) 2.2 ppm (s, 0.5H). TGA (air, 1000 °C): found, 28.5%; calcd, 31.2%. $T_{d5\%}$ = 360 °C. GPC: M_n = 1591; M_w = 1862; PDI = 1.17

Peroxide Oxidation of Silica Core. A 3.0 g sample of phenylsilsesquioxane derivative, 2.5 g of KF, and 2.0 g of $NaHCO_3$ were added to a 250 mL round-bottom flask. Then 25 mL of THF was added and the mixture stirred until the silsesquioxane dissolved. Then, 25 mL of methanol and 20 mL of 30% H_2O_2 were added, whereupon the silsesquioxane precipitated. This mixture was then refluxed for 4 h over which time the solution became clear yellow and later precipitated white silica. The solution was then decanted to remove the silica and extracted with ethyl acetate/water three times in order to remove salts. The water layers were combined and extracted with addition ethyl acetate to ensure complete capture of any organic compounds. The combined organic layers were dried over sodium sulfate and evaporated to remove the solvents. The residual mixture was analyzed by GC−MS, ^1H NMR, or ^{13}C NMR.

Results and Discussion

The first step in the development of poly(bromooctaphenylsilsesquioxane)s, Br_xOPS, was to delineate the bromine substitution pattern and optimize bromination conditions. Thereafter efforts were made to demonstrate the general utility of $Br_{5.3}OPS$ for the synthesis of 3-D polyfunctional molecules using standard catalytic cross-coupling reactions. The rationale for choosing $Br_{5.3}OPS$ derives from the complex bromination patterns identified, as discussed below.

Bromination Patterns. The extent of bromination increases with increases in equivalents of Br_2 added until an average of ≈16 bromines per molecule is reached. At this point, product solubility decreases significantly, hindering further substitution. The average degree of substitution (x) was found to be reproducible to within 0.5 Br/molecule for all extents of substitution if finely ground OPS powder was used. The breadth of the distribution generally decreased with increasing substitution, especially as x approached 16 and the higher-substituted materials precipitated. The larger breadths at low substitution likely occur because of the greater importance of the initial heterogeneous stage of the reaction, where OPS molecules that dissolve first can react with more bromine than those that dissolve later. All Br_xOPS materials tested had similar solubilities and could not be separated by column chromatography.

The extent of bromination vs equivalents of bromine added was followed two ways. First ^1H NMR was used to determine the total number of aryl protons vs an internal standard (THF), providing information as to the extent of substitution, Table 1. These values were corroborated by MALDI−TOF mass spectroscopy, Figure 1, which shows a series of peaks separated by 79 amu consistent with the proposed structure.

MALDI−TOF calculated values for average degrees of substitution were consistently higher than calculated from ^1H NMR. This is likely due to increases in ionization potential for the more brominated Br_xOPS, increasing their relative fraction in the MALDI−TOF spectra. MALDI−TOF spectra unambiguously confirm retention of the silica core throughout the reaction.

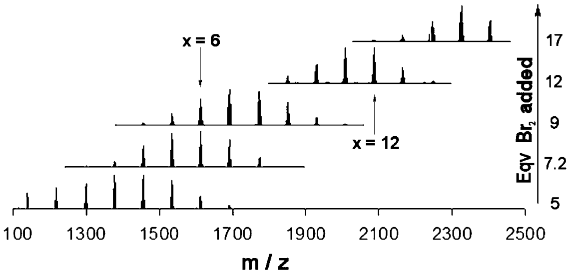


Figure 1. Bromines per OPS molecule vs equivalents of Br_2 added as determined by MALDI−TOF.

Table 1. Bromines per OPS by ^1H NMR and MALDI−TOF

molecule	equiv of Br_2 added	bromines (^1H NMR)	bromines (MALDI-TOF)	std dev
$Br_{3.1}OPS$	5	3.10	3.6	1.6
$Br_{5.3}OPS$	7.2	5.31	5.7	1.3
$Br_{6.6}OPS$	9	6.59	7.2	1.4
$Br_{10.8}OPS$	12	10.77	11.8	1.3
$Br_{15.7}OPS$	17	15.68	15.9	0.6

Table 2. GPC and TGA Characterization Data for Various Extents of Bromination

	$Br_{5.3}OPS$	$Br_{10.7}OPS$	$Br_{15.7}OPS$
isolated yield (%)	83	77	57
M_n	921	1451	1544
M_w	928	1489	1562
PDI	1.01	1.03	1.01
% ceramic yield (1000 °C)	32.4	24.5	19.5
% yield calcd	33.1	25.5	21.1
5% T_d (°C)	420	435	440

Three halogenated solvents were assessed as to their effects on substitution distribution patterns. CH_2Cl_2 provides much narrower distributions than $CHCl_3$ or CCl_4, owing to the lower solubility of OPS in these solvents. The use of Fe, $FeCl_3$, or $FeBr_3$ catalysts gave similar results.

The Br_xOPS materials were further characterized by GPC and TGA; see Table 2. As expected, GPC shows narrow polydispersities because of similar hydrodynamic volumes confirming the absence of ring-opening polymerization and retention of intact silica cores. Also as expected, GPC calculated molecular weights are lower than those derived from ^1H NMR and MALDI−TOF due to their spherical shape and rigidity as compared to the linear polystyrene calibration standards used. One interesting qualitative observation is that GPC samples had to be diluted more than normal because of the high refractive indices of the polybrominated cubes. TGA values are also consistent with the proposed structures. Thermal decomposition temperatures increase with increases in Br content pointing to improved thermal stability.

The complex nature of the ^{13}C and ^1H NMR spectra of Br_xOPS indicates the presence of multiple isomers at all extents of bromination. However the broad peaks observed, in part caused by steric congestion around the silsesquioxane coupled with the unknown influence of the silica cage on chemical shifts, made identification and quantification of individual isomers very difficult. In an effort to characterize the Br_xOPS substitution patterns, the Si−C bonds were cleaved using tetrabu-

Table 3. (TBA)F Cleavage Reaction of $Br_{15.7}OPS$ ^1H NMR Data

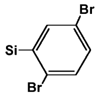
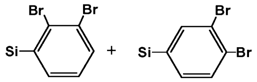
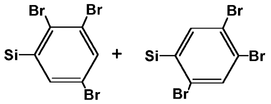
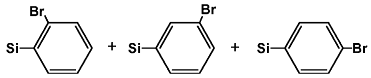
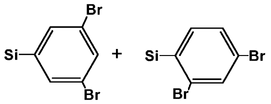
^{1}H-NMR Peak	Assignment	Mol Percent (± 2%)	Isomer on BrOPS
7.36	1,4-dibromobenzene	77%	
7.62	1,2-dibromobenzene	12%	
7.77	1,2,4-tribromobenzene	6%	
7.24, 7.48	bromobenzene	3%	
7.67	1,3-dibromobenzene	2%	

Table 4. Distribution of Isomers from KF/H_2O_2 or (TBA)F Cleavage

$Br_{5.3}OPS$		$Br_{10.8}OPS$		$Br_{15.7}OPS$	
major isomers	mole fraction[a] (%)	major isomers	mole fraction[a] (%)	major isomers	mole fraction[a] (%)
4-bromo	39	4-bromo	44	2,5-dibromo	77
phenyl	37	2,5-dibromo	39	other dibromo	14
3-bromo	15	other dibrominated	8	monobromo	3
2-bromo	6	phenyl	9	tribrominated	6
dibrominated	3	3-bromo	<1		

*± 3%.

tylammonium fluoride ((TBA)F) to generate Si−F and Ar−H bonds. The resulting organic fragments were extracted and analyzed by NMR and GC−MS.

Table 3 shows the distribution of isomers resulting from (TBA)F cleavage of $Br_{15.7}OPS$. The predominant isomer found was 1,4 dibromobenzene, which could only result from 2,5 substituted silsesquioxanes (ortho−meta). Unfortunately, because this reaction replaces the silicon atom of the cage with a hydrogen atom; determination of the position of the bromine on singly brominated species was impossible. To resolve this issue, we used KF/H_2O_2 cleavage to produce Si−F and Ar−OH bonds.[17] The resulting phenols could then be extracted and analyzed by ^1H or ^{13}C NMR, but with retention of information regarding the position of the silicon atom.

Peroxide cleavage of $Br_{5.3}OPS$ provides detailed information about the isomeric distribution of the bromines on monofunctionalized rings. Table 4, combines the results of both methods. Surprisingly, initial bromination occurs predominantly in the para position, in contrast to the ortho−meta substitution of the difunctional rings.

To further understand these seemingly contradictory results, $Br_{10.8}OPS$ was analyzed by both (TBA)F and peroxide cleavage. We find that the dibrominated rings were again mostly 2,5-substituted, whereas for the mono-brominated moieties, only the *para* isomer was observed. It is known that during bromination of common arenes, both intramolecular and intermolecular rearrangements occur.[18] The most reasonable explanation for the phenomena observed here is that a catalyst mediated equilibration occurs between the three monobromophenyl isomers and excess bromine, such that the meta and ortho isomers react preferentially to form the more stable 2,5-dibrominated species, while the para isomer dibrominates relatively slowly as compared to its rate of rearrangement to meta or ortho.

The equilibration process was probed by adding two different Br_xOPS materials together in CH_2Cl_2 saturated with HBr, using $FeBr_3$ as catalyst. If intermolecular rearrangement occurs, transfer of bromines should result in a material with a value x, intermediate between the two starting species. This experiment was performed with $Br_{3.1}OPS$ and $Br_{15.7}OPS$. However, little intermolecular rearrangement was observed after 24 h, indicating that bromine transfer is predominately intramolecular in nature.

Polyfunctionalization of $Br_{5.3}OPS$. Once the details of the bromination process were completely worked out, it became possible to explore the use of Br_xOPS compounds as nanoconstruction sites using a wide variety of catalytic coupling reactions[19−22] including Heck, Suzuki, and Sonogashira methods, which can often be effected at room temperature. The goal was to demonstrate access to numerous new polyfunctional nanosized macromonomers per Scheme 2 and Table 5. In these studies, $Br_{5.3}OPS$ was used to ensure that the products were primarily para-substituted and to reduce the potential to form unwanted (for the current purposes) disubstituted phenyl rings. Reactions i and iii have been optimized for yields and conversion, as will be reported in more detail shortly.

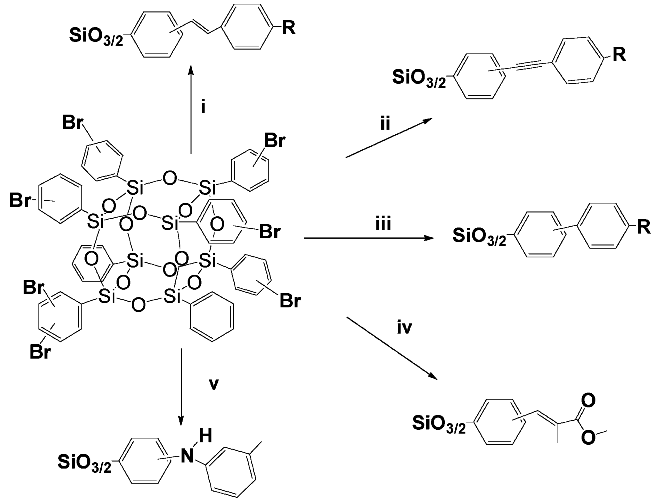
It is important to note that it is in principle possible to prepare wholly para-substituted phenyl silsesquioxanes via reaction of the Grignard salt of the appropriate para-substituted bromobenzene with either $SiCl_4$ or $Si(OR)_4$, followed by condensation to the silsesquioxane.[23]

Table 5. Characterization Data for $Br_{5.3}$OPS Derivatives

		GPC			TGA		MALDI-TOF (Ag^+ adduct)		
cmpd	% convn[a]	M_n	M_w	PDI	% found	% calcd	most common isotope	found	calcd
$Br_{5.3}$OPS		921	928	1.01	32.4	33.1	$Br_6Si_8O_{12}C_{48}H_{34}$	1614.1	1614
i	99	1669	1786	1.07	27.0	29.2	$Si_8O_{12}C_{48}H_{34}(C_9H_9)_6$	1839.4	1838
ii	51	1118	1194	1.07	30.3	31.1	$Si_8O_{12}C_{48}H_{34}(C_9H_7)_4Br_2$	1754.8	1755
iii	99	1983	2027	1.02	32.6	33.5	$Si_8O_{12}C_{48}H_{34}(C_6H_5)_6$	1597.3	1597
iv	99	2450	3015	1.23	28.3	30.8	$Si_8O_{12}C_{48}H_{34}(C_5H_7O_2)_6$	1728.8	1729
v	63	1591	1862	1.17	28.5	31.2	$Si_8O_{12}C_{48}H_{34}(C_7H_8N)_4Br_2$	1718.0	1718

[a] Conversion represents the fraction of aryl bromides reacted in the final product.

Scheme 2. Synthesis of Br_xOPS Derivatives[19−22]



However, the yields for these types of reaction are typically very poor and the hydrolysis process for the production of discrete silsesquioxane cages is not trivial. The current approach is much easier, with much higher yields but at the expense of product uniformity.

Reaction i of Scheme 2 leads to *p*-stilbene substituted silsesquioxanes that exhibit UV−vis absorption behavior nearly identical to stilbene but highly red-shifted 60−80 nm (0.6−0.8 eV) emissions with solution luminescence quantum efficiencies (Φ_{PL}) of 30−60% vs Φ_{PL} = 5% for stilbene. The reaction proceeds quantitatively at room temperature after 48 h by MALDI−TOF analysis. No residual bromine was detected by MALDI−TOF or GC−MS of fluoride-cleaved organic fragments as will be described in detail in a separate paper.[24]

Reaction ii provides both *p*-alkyne substituents and coincident formation of akenyl bromides, as evidenced by an alkenyl C−H peak at 6.5 ppm in the NMR. MALDI−TOF data indicates an average degree of substitution of 7.5 whereas the starting material was 5.3 (Table 5). Thus, the intermediate alkenyl bromide reacts with a second alkyne, in theory leading to star oligoacetylenes, as will be reported elsewhere.

Reaction iii provides facile access to a variety of biphenyl and terphenyl-functional silsesquioxanes,[24] similar to those reported recently to form via Grignard reactions.[25] Suzuki chemistry and its variants allows for milder conditions that do not destroy the cage structure, according to MALDI−TOF and GPC analysis. These materials are suggested to behave like organic quantum dots.[25]

Reaction iv provides polymerizable functionality for spin-on coatings. It can be run coincident with reactions i−iii to provide mixed functionality to form, for example, cross-linkable emitting or transport layers for organic electronics.

Reaction v provides alternative access to polyaniline derivatives similar to those described before[13,14] but allowing modification of the nitrogen to afford changes in solubility, miscibility, or thermal, mechanical and/or photonic properties. Furthermore, the products are primarily para rather than meta.[13,14]

Finally, it is important to note that the Br_{16}OPS derivatives in general offer the same reactivity as $Br_{5.3}$-OPS leading to R_{16}OPS materials, as we will discuss in a later paper.[24]

Conclusions

In conclusion, octaphenylsilsesquioxane was found to brominate rapidly using molecular bromine in dichloromethane. The average extent of bromination could be controlled by reaction stoichiometry, with narrow distributions of bromines per molecule. The first substitution was found to be primarily in the para position relative to the silicon. However, subsequent intramolecular rearrangements allowed the 2,5-dibrominated species to be the major multiply substituted isomer. These brominated phenyl silsesquioxanes were then found to react under a several standard coupling conditions (Heck, Suzuki, etc.) to form a variety of hybrid inorganic−organic materials, which will be the basis of further reports.

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