para-Octaiodophenylsilsesquioxane, [*p*-$IC_6H_4SiO_{1.5}$]$_8$, a Nearly Perfect Nano-Building Block

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ABSTRACT The cubic symmetry of octafunctional octaphenylsilsesquioxanes [ROPS, $(RC_6H_4SiO_{1.5})_8$] coupled with a 1 nm diameter offers exceptional potential to assemble materials in three dimensions with perfect control of periodicity and the potential to tailor global properties at nanometer length scales. OPS itself is very inert and insoluble and can only be functionalized *via* electrophilic reactions with difficulty and with poor substitutional selectivity. However, functionalized OPS products are robust and highly soluble, offering easy purification and processing. In contrast to previous studies, we report here that OPS reacts with ICl at sub-ambient temperatures to provide (following recrystallization) [*p*-$IC_6H_4SiO_{1.5}$]$_8$, or I_8OPS, in good yields and with excellent selectivity: >99% mono-iodo substitution with >93% para substitution as determined by H_2O_2/F^- cleavage of the Si−C bonds to produce iodophenols. I_8OPS in turn can be functionalized using conventional catalytic coupling reactions to provide sets of >93% para-substituted, functionalized compounds (alkynes, alkenes, aryl amines, phosphonates, aryl amines, polyaromatics, *etc.*), suggesting the potential to develop diverse nano-building blocks for the assembly of a wide variety of materials, some with novel photonic, electronic, and structural properties.

KEYWORDS: nano-building blocks · silsesquioxanes · 3-D cubic symmetry · octafunctional · octaiodophenylsilsesquioxane

The perfect assembly of two- and three-dimensional (2-D and 3-D) structures from molecular components or nano-building blocks is of immense current interest because of the potential to realize novel properties in nanosized materials and to tailor global properties perfectly by manipulation of component organization at the finest length scales. Such assembly requires components that fulfill the mathematical relationships found for Bravais lattices. The higher the component symmetry, the higher the probability of minimizing defects in assembled 2- and 3-D structures, given that misaligned but highly symmetrical components would require the least energy (associated with the least movement) to reorient, aligning with adjacent assembled components.[1]

In this light, there is great need for highly symmetrical nano-building blocks that offer diverse and easily modified functionality, permitting selective assembly with the objective of tailoring global properties through manipulation of features at nanometer length scales. While there are numerous literature examples of highly symmetrical 2-D molecules, a much smaller number of molecules offer highly symmetrical 3-D functionality, including tetrahedranes, cubanes, and star molecules.[1−8] Recent work by Hawthorne *et al.* describes access to dodeca-functional 3-D carborane derivatives.[9,10] However, to our knowledge, few molecular structures offer perfect (cubic) symmetry in three dimensions and octafunctionality such that each octant in Cartesian space contains one functional group. These structures include the very difficult to prepare cubane family of compounds[1−3] and the easily prepared cubic silsesquioxanes (SQs), Q_8 [$RMe_2SiOSiO_{1.5}$]$_8$ and T_8 [$RC_6H_4SiO_{1.5}$]$_8$, or polyhedral oligomeric silsesquioxane (POSS) materials.[11−52] In principle, these compounds offer the potential to assemble macroscopic structures nanometer-by-nanometer in two or three dimensions.

We and others are exploring the utility of SQs as novel materials in their own right and for nanometer-by-nanometer assembly of macroscopic shapes. Thus, SQs based on [$RMe_2SiOSiO_{1.5}$]$_8$, where R = H, vinyl, or epoxy groups, permit nanometer tailoring in nanocomposites.[11−52] Several groups have also examined [vinyl$SiO_{1.5}$]$_8$ as a starting point for highly symmetrical molecules,[53−65] but only a few examples have been directed toward materials synthesis.[53−55] In an effort to develop robust octafunctional nano-building blocks, we initiated studies on the related T_8 systems, (RPhenyl$SiO_{1.5}$)$_8$, where R = NH_2 (from R = NO_2) and Br, produced by electrophilic substitution of octaphenylsilsesquioxane (OPS), or (HPhenyl$SiO_{1.5}$)$_8$.[48−50,52,57] Un-

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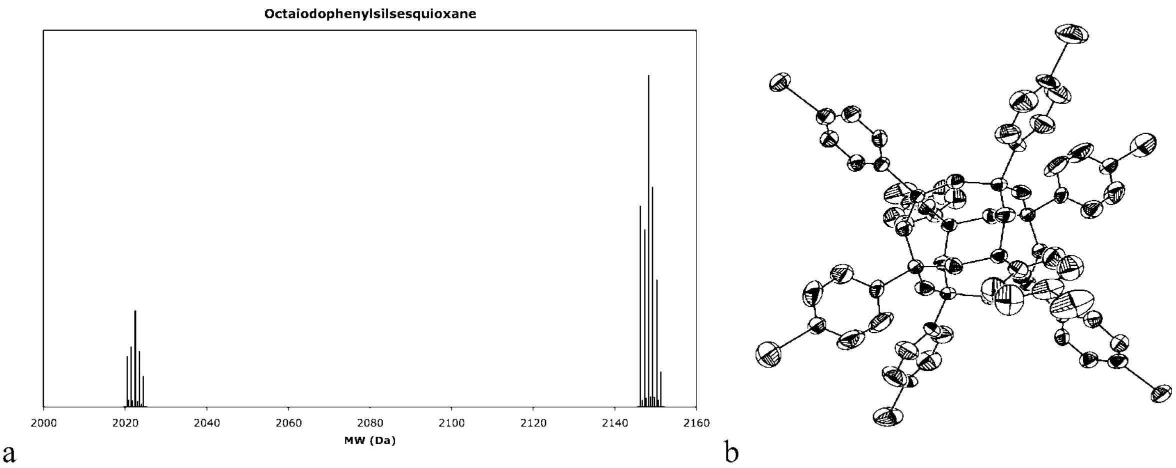


Figure 1. Recrystallized I_8OPS: (a) MALDI-TOF sprectrum and (b) single-crystal structure. Note that MALDI uses a 370 nm laser that ionizes C—I bonds, cleaving them and leading to spurious peaks at 2021–2027 Da.

fortunately, electrophilic substitution often gives limited substitutional selectivity.

For example, OPS nitration in fuming nitric acid gives a 65:20:15 meta:ortho:para mixture of $(NO_2phenylSiO_{1.5})_8$, whereas bromination gives a 65:20:15 para:ortho:meta mixture. Thus, the opportunity to elaborate on these materials to give perfectly symmetrical functionality appears impossible. Although it is possible to successfully tailor global properties at nanometer length scales with these symmetrically defective nano-building blocks through careful choice of the assembly chemistries,[47−50] it is still highly desirable to avoid introducing defects at the earliest stage of functionalization. Thus, we were surprised to discover that iodination of OPS with ICl at −40 °C (see Experimental Section) gives a product that is 90% I_8OPS. Subsequent recrystallization from hot ethyl acetate to remove the I_9 isomer gives product that is ≥99% octa-substituted and ≥93% para-substituted (see Figure 1, Table 1, and Supporting Information) in 30−40% yield. We report here initial efforts to develop diverse functionality (tools) for eventual use in producing stars, core–shell materials, novel dendrimers, and low-defect-density nanocomposites (subject to the effects of $T\Delta S$).

Given that haloaromatics are well-known starting points for further modification of aromatic rings using traditional Heck, Songashira, Stille, and Suzuki chemistries,[66,67] efforts were made to modify I_8OPS using these traditional coupling methods. Scheme 1 illustrates a basic set of reactions undertaken to demonstrate the versatility of I_8OPS as a starting point for the production of 3-D nano-building blocks. The resulting compounds were characterized using a variety of techniques, with the results summarized in Table 1.

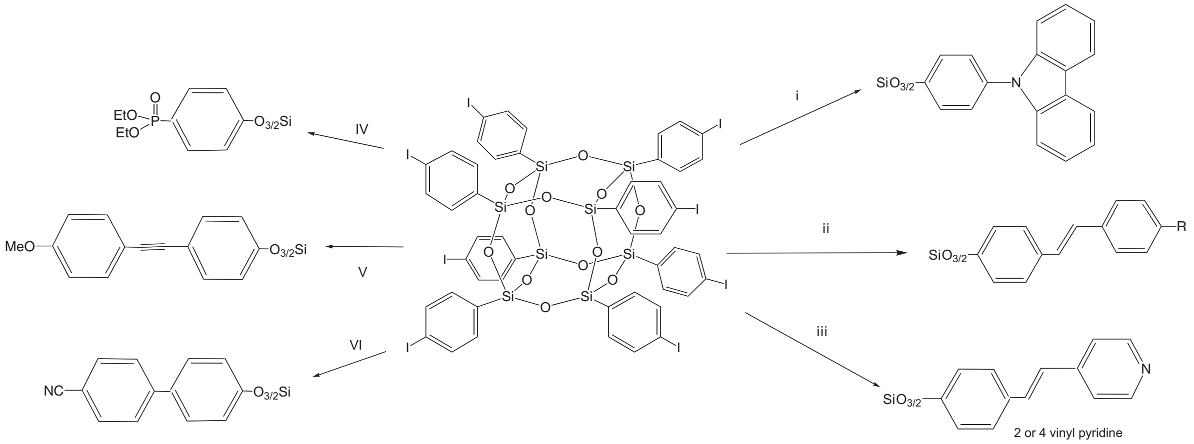
Although the yields and conversions are quite high, there is still room for improvement. The ability to effect 100% conversion of all eight aryl iodides to the functional groups shown is necessary to develop minimal-defect 3-D nanostructures by covalent, electrostatic, or dative bonding.

Only the alkynes and stilbenes are obtained easily with 100% conversion. We believe it will also be possible to obtain 100% conversions for the other compounds shown in Scheme 1 with further refinement of

TABLE 1. Product Yields, Conversions, GPC, and MALDI-TOF Data for Scheme 1 Compounds

			GPC		CY (%)[c]		MALDI (Da)	
compound	yield[a] (%)	% conv H_2O_2/F^-[b]	M_n (Da)	PDI	calcd	found	calcd	found 100% intensity
I_8OPS	90	99[e]	1159	1.01	23.5	18.8	2148.57 (Ag^+)	2148 (100%)
4-biphenyl	83	93	1052	1.01	25.4	24	1750.19 (Ag^+)	1749 (100%)
4-(4-cyanobiphenyl)	64	88	1556	1.08	26.0	26		
4-4(-MeOPh ethyne)	85	99	1327	1.01	22.6	23.8		
4-stilbene	91	99+	1609	1.02	26.0	22	1958.49 (Ag^+)	1958 (100%)
4-(methyl stilbene)	87	99	1620	1.04	24.4	22	2070.69 (Ag^+)	2071 (100%)
4-*N*-carbazole	76	92	2516	1.2	20.4	23		
4-(4-vinylpyridyl)	48	90	1454	1.02	25.9	22	1858.5 (+)	1858 (100%)
4-(2-vinylpyridyl)	50	91	1513	1.02	25.9	20	1858.5 (+)	1858 (100%)
4-diethyl phosphonate	81		1086	1.01	49.4[d]	56	2128.2 (Li^+)	2128 (100%)

[a] Isolated yield calculated relative to complete conversion of aryl iodide. [b] Conversion calculated relative to unreacted aryl iodide. [c] Ceramic yield in air/10 °C/min. [d] Conversion assumes product is $SiO_2 \cdot 0.5P_2O_5$ phosphosilicate glass. [e] Conversion to aryl iodide.



Scheme 1. Functionalization of I_8OPS using traditional coupling chemistries (see Experimental Section).[66,67]

synthetic procedures, given that only unreacted iodide remains.[68] Even with 100% conversion, assembly in three dimensions will generate defect structures when the substitution patterns are not perfect.

Efforts to determine the extent of para-substitution focused on H_2O_2/F^- cleave of the Si−C bonds to produce phenolic cleavage products.[52,69–71] Thus, for example, cleavage of the octastilbene derivative provides a product that is >95% 4-hydroxystilbene, 2–3% 3-hydroxystilbene, and <1% 2-hydroxystilbene as determined by GC/MS. This is in accord with the H_2O_2/F^- phenolic products obtained from I_8OPS and the pyridine derivatives.[72] Given that the crystallization process is well-known to self-select for purity,[73] we believe that assembly of low-defect-density 3-D structures is accessible using the types of compounds that can be synthesized from I_8OPS. Thus, these materials and related analogues may still serve as "perfect" 3-D nano-building blocks.

Brief comments about the ceramic yields (CY) given in Table 1 are warranted. First, the CY (to SiO_2) for I_8OPS in air is expected to be 23.5%. However, the CY is found to be only 18.8%. This suggests that there is some competitive sublimation of the compound during heating, which may explain the low CYs found for most of the compounds. An alternative perspective suggests that these compounds may be suitable for vapor deposition processing. Three exceptions are the alkyne, phosphonate, and carbazole compounds. As we will report elsewhere, the alkyne systems polymerize to give 3-D carbon networks that are air stable to temperatures >550 °C and may not completely oxidize in the time frame of the thermogravimetric analysis (TGA), as evidenced by dark residues after the TGA runs rather than white SiO_2.[68] The phosphonate system can be expected to decompose to give phosphosilicate glasses that encapsulate residual carbon, leading to the much higher CYs than expected.[74] Finally, the carbazole system, which has the poorest conversion, retains the highest aryl iodide content, and the decomposition process(es) may lead to more char that also limits oxidation at the heating rates used for our standard TGA runs.

All of these materials are highly soluble and offer oxidative stabilities >400 °C (TGA), especially the alkyne complexes, as noted above.[68] Of particular interest are the cyano and 4-vinylpyridine moieties, which offer the potential for 3-D dative bonding.[74] The 2-vinylpyridine system may provide access to octairidium systems that are of potential use in light-emitting diodes, light harvesting, and novel photovoltaics.[75–79] Finally, while the UV–vis absorptions of the stilbene derivatives are essentially the same as those of the parent organic molecules, the emission characteristics of the derivatives are very different, being red-shifted up to 80 nm (0.75 eV), as will be discussed elsewhere [M. Neurock, J.-S. Filhol, C.-Y. Lee, R. M. Laine, C. Brick, and M. Roll, unpublished work].

CONCLUSIONS

Iodinated OPS, showing eight or nine iodines per molecule, may be synthesized in 100 g quantities with >90% yields. Subsequent, careful recrystallization allows isolation of highly crystalline, octaiodinated OPS, which shows ≥93% selectivity for para substitution, in ~30–40% overall yield. This compound offers nearly perfect cubic symmetry and allows the addition of diverse functional groups. In their own right, these nanosized molecules show novel properties that are more than the sum of the individual components. The high degree of symmetry, coupled with the ability to tailor the functionality at the points of highest symmetry, suggests that these molecules also offer potential to create 3-D network structures with a minimum numbers of defects. Viewed from another perspective, their assembly offers the potential to create organic/inorganic nanocomposites with complete tailoring of global properties at nanometer length scales. From another vantage point, they might also offer novel opportunities to modify the surfaces of other structures with similar goals in mind. Future publications will address these possibilities.

EXPERIMENTAL SECTION

Materials. OPS was prepared using literature methods[80] or was a gift from Mayaterials.com. Cyanophenylboronic acid was prepared using the method of Li *et al.*[81] ICl, 1.0 M in dichloromethane, *N*-methyldicyclohexylamine, tri-*o*-tolylphosphine, phenylboronic acid, and other synthetic reagents were purchased from Sigma-Aldrich and used as received. Silver oxide was purchased from F&M Scientific and was ground and oven dried and cooled under nitrogen prior to use. Pd_2dba_3 was purchased from Strem Chemicals. Dichloromethane was purchased from Burdick-Jackson. Solvents were dried over 4 Å molecular sieves. Dioxane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen.

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

Nuclear Magnetic Resonance. All ^{1}H NMR spectra were obtained in $CDCl_3$ and recorded on a Varian INOVA 400 MHz spectrometer. ^{1}H spectra were collected at 400 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.

Thermogravimetric Analyses. All thermogravimetric/differential thermal analyses were run on a simultaneous DTA−TGA instrument (model 2960, TA Instruments, Inc., New Castle, DE). Samples (15–25 mg) were loaded in alumina pans and ramped at 10 °C/min to 1000 °C in dry air at a flow rate of 60 mL/min.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Spectrometry. MALDI-TOF studies were done on a Micromass TofSpec-2E instrument equipped with a 337 nm nitrogen laser in positive-ion reflectron mode using poly(ethylene glycol) as a calibration standard, dithranol as the matrix, and $AgNO_3$ as the ion source. Samples were prepared by mixing solutions of 5 parts matrix (10 mg/mL in THF), 5 parts sample (1 mg/mL in THF), or optionally 1 part $AgNO_3$ (2.5 mg/mL in water) or 1 part LiOTf (2.5 mg/mL in water) and blotting the mixture on the target plate.

Gas Chromatography/Mass Spectroscopy. GC/MS data were recorded on a Thermo/electron TraceMS instrument using splitless injection. This was accomplished by the reaction of 0.8 mL of MeOH/H_2O/NH_4F solution with 10 mg of sample in 1.5 mL of THF at 60 °C/2 h. The resulting reaction mixture was quenched by the addition of 5 mL of saturated brine. The organic layer was extracted, dried with sodium sulfate, and subsequently injected into the instrument.

UV–Vis Spectroscopy. Absorption and emission spectra were obtained using a Fluoromax-2 fluorimeter at an excitation wavelength of 320 nm. Samples for UV–vis spectroscopy were typically made at concentrations of $10^{-5}-10^{-6}$ M to avoid exciplex formation and fluorimeter detector saturation.

Synthetic Methods. ***Synthesis of Octaiodophenylsilsesquioxane.*** To an oven-dried, single-neck 1 L flask under flowing N_2 was added 290 mL of 1.0 M ICl/CH_2Cl_2 solution. The solution was cooled to −40 °C using a dry ice/ethanol/ethylene glycol bath, and 26.7 g (25.8 mmol) of powdered OPS was added at an approximate rate of 5 g/min with stirring. HCl evolution began within 1 min of OPS addition. Flowing N_2 flushed the HCl from the reaction system. Residual OPS, sticking to the sides of the flask, was washed into the reaction solution with 40 mL of CH_2Cl_2. The reaction was stirred for 24 h at −40 °C, allowed to warm to room temperature with stirring over another 24 h, and quenched with 300 mL of ~1 M sodium metabisulfite.

When all the ICl was consumed and quenched, the organic layer was extracted, washed three times with water, filtered, and dried over anhydrous sodium sulfate. The volume was subsequently reduced by rotary evaporation to produce a white solid. This solid was further dried under vacuum and then redissolved in 400 mL of THF. This clear solution was then precipitated into 3 L of cold methanol, providing a white powder that was then vaccuum-dried to give 47 g (23 mmol, 90% yield). The as-precipitated material could then be recrystallized from hot ethyl acetate to give colorless crystals (~30−40% yield). Material was subsequently characterized as described in Table 1 and Supporting Information. Single crystals suitable for X-ray diffraction were grown in using the same recrystallization procedures on a smaller scale.

General Heck Reaction Conditions.[82] To an oven-dried 50 mL Schlenk flask under N_2 was added 1.00 g (0.48 mmol, 3.9 mmol phenyl) of recrystallized I_8OPS, followed by 108 mg (0.175 mmol) of Pd_2dba_3 and 288 mg (0.788 mmol) of tri-*o*-tolylphosphine, and then 2.00 g (29.8 mmol) of granular copper metal. *N*-Methyldicyclohexylamine (3 mL, 14 mmol), 4-methylstyrene (2.8 mL, 22 mmol), and 15 mL of dioxane were added sequentially by syringe. The reaction mixture was then heated at 95 °C for 18 h with stirring under nitrogen. Thereafter, the cooled mixture was filtered through a 1 cm Celite column and precipitated into 75 mL of cold methanol. The resulting solid was filtered off, redissolved in 7.5 mL of ethyl acetate, filtered through another 1 cm Celite column, and precipitated into 75 mL of cold methanol. The resulting white solid was vacuum-dried for 4 h, yielding 0.84 g (0.45 mmol, 87% yield) of white material. Material was subsequently characterized as described in Table 1 and Supporting Information.

General Suzuki Reaction Conditions.[83] To an oven-dried 50 mL Schlenk flask under N_2 was added 1.00 g (0.48 mmol, 3.9 mmol phenyl) of recrystallized I_8OPS, followed by 70 mg (0.069 mmol) of Pd_2dba_3 and 168 mg (0.46 mmol) of tri-*o*-tolyl phosphine, phenylboronic acid (970 mg, 7.8 mmol), and silver(I) oxide (1.6 g, 0.46 mmol). Distilled THF (15 mL) was added by syringe, and the reaction was stirred under N_2 at ambient for 18 h. Thereafter, the mixture was filtered under vacuum to remove the Ag_2O particles and subsequently precipitated into 75 mL of methanol. The resulting off-white solid was then recovered by filtration, redissolved in 7.5 mL of ethyl acetate, filtered through another 1 cm Celite column, reprecipitated into 75 mL of cold methanol, and vacuum-dried for 4 h, giving 0.67 g (0.4 mmol) of white powder with an 83% yield.

General Carbazole Amination Conditions.[83] To an oven-dried 50 mL Schlenk flask under N_2 was added 0.50 g (0.24 mmol, 1.95 mmol phenyl) of recrystallized I_8OPS, followed by 360 mg (2.1 mmol) of carbazole, copper(I) oxide (420 mg, 0.46 mmol), and 5 mL of *N*,*N*-dimethylacetimide. The mixture was heated with stirring at 150 °C under N_2. After 6 h, an additional 360 mg of carbazole and 420 mg of Cu(I) oxide were added, and stirring was continued for another 14 h, followed by cooling to ambient. The reaction mixture was then filtered through a 1 cm Celite column and precipitated into 75 mL of cold methanol. The resulting solid was filtered off, redissolved in 7.5 mL of ethyl acetate, filtered a second time through Celite, and reprecipitated using 75 mL of cold methanol. After vacuum drying, 0.44 g (0.345 mmol) of powder was obtained, consisting of a mixed substitution product. Material was subsequently characterized as described in Table 1 and Supporting Information.

General Vinylpyridine Reaction Conditions.[82] To an oven-dried 50 mL Schlenk flask under N_2 was added 1.00 g (0.48 mmol, 3.9 mmol phenyl) of recrystallized I_8OPS, followed by 72 mg (0.156 mmol) of Pd_2dba_3, 192 mg (0.627 mmol) of tri-*o*-tolylphosphine, and 300 mg (1.63 mmol) of copper/tin alloy (H_2CuSn). Thereafter, Et_3N (2.2 mL, 14.1 mmol), 2-vinylpyridine (2.5 mL, 22 mmol), and 30 mL of dioxane (60 mL for 4-vinylpyridine) were added by syringe.

The reaction mixture was heated to 90 °C under N_2 for 18 h and then allowed to cool to room temperature. The reaction mixture was filtered through 1 cm of Celite and precipitated into 75 mL of hexane/cyclohexane (50:50 v/v). The resulting solid was recovered by filtration, redissolved in 25 mL of THF/toluene, and washed successively with 25 mL portions of saturated brine, 0.1 M $NaHSO_3$, 0.1 M $NaHCO_3$, and water. The organic layer was dried over sodium sulfate, and solvent was removed by rotary evaporation. Thereafter, the recovered solid was dissolved in 7.5 mL of ethyl acetate and precipitated into 75 mL of hexane/cyclohexane (50:50 v/v), providing 440 mg (0.236 mmol, 49% yield) of off-white powder. Material was subsequently characterized as described in Table 1 and Supporting Information.

Phosphonation of I_8OPS.[84] To an oven-dried 50 mL Schlenk flask equipped with a reflux condenser under N_2 was added 1.00 g (0.48 mmol, 3.9 mmol phenyl) of recrystallized I_8OPS, followed by 28 mg (0.039 mmol) of tetrakis(triethylphosphite) Ni(0) and 8 mL of *m*-xylene. Triethylphosphite (1.0 mL, 6.25 mmol) was then added by syringe. The mixture was heated to reflux with stirring for 24 h. After cooling, the reaction mixture was added to 150 mL of cold hexane to precipitate the product. The precipitate was filtered off, redissolved in 7.5 mL of toluene, and reprecipitated into 100 mL of cold hexane. The precipitate was filtered to give 720 mg (0.33 mmol, 68% yield) of white product. Material was subsequently characterized as described in Table 1 and Supporting Information.

General Sonogashira Reaction Conditions from I_8OPS.[85] To a dry 50 mL Schlenk flask under N_2, equipped with a magnetic stir bar, were added 0.5 g (2.4 mmol) of I_8OPS, 0.29 mL (2.6 mmol) of phenylacetylene, 18.2 mg (0.096 mmol, 4%) of CuI, 194 mg (0.168 mmol, 7%) of tetrakis(triphenylphosphine)palladium(0), 5.0 mL of 1,4-dioxane (previously distilled and degassed), and 0.808 mL (4.9 mmol) of triethylamine. The solution was stirred at 60 °C for 24 h. The solution turned dark gray-brown. The mixture was passed through a short Celite column and poured into an excess of methanol to deactivate the catalyst. The resulting precipitate was collected by filtration. The residue was redissolved in 5.0 mL of ethyl acetate and precipitated into 100 mL of methanol. The light brown-orange powder was collected by filtration and dried *in vacuo* for 5 h, giving 0.50 g (90% yield) of product. Material was subsequently characterized as described in Table 1 and Supporting Information.

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Supporting Information Available: Relevant NMR and FTIR data, description of structure determination, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and a CIF file for I_8OPS. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Detken, A.; Zimmermann, H.; Haeberlen, U.; Poupko, R.; Luz, Z. Molecular Reorientation and Self-Diffusion in Solid Cubane by Deuterium and Proton NMR. *J. Phys. Chem.* **1996**, *100*, 9598–9604.
2. Eaton, P. E. Cubane: Starting Materials for the Chemistry of the 1990s and the New Century. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421–1436.
3. Yildrim, T.; Gehring, P. M.; Neumann, D. A.; Eaton, P. E.; Emrick, T. Solid Cubane: A Brief Review. *Carbon* **1998**, *36*, 809–815.
4. Ganesan, P.; Yang, X.; Loos, J.; Savenije, T. J.; Abellon, R. D.; Zuilhof, H.; Sudhölter, E. R. R. Tetrahedral n-Type Materials: Efficient Quenching of the Excitation of p-Type Polymers in Amorphous Films. *J. Am. Chem. Soc.* **2005**, *127*, 14530–14531.
5. Seidel, S. R.; Stang, P. J. High-Symmetry Coordination Cages via Self-Assembly. *Acc. Chem. Res.* **2002**, *35*, 972–983.
6. Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. Synthesis, Spectroscopy, and Morphology of Tetrastilbenoidmethanes. *J. Am. Chem. Soc.* **1998**, *120*, 2987–2988.
7. Robello, D. R.; Andre, A.; McCovick, T. A.; Kraus, A.; Mourey, T. H. Synthesis and Characterization of Star Polymers Made from Simple, Multifunctional Initiators. *Macromolecules* **2002**, *35*, 9334–9344.
8. Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. Synthesis, Morphology, and Optical Properties of Tetrahedral Oligo(phenylenevinylene) Materials. *J. Am. Chem. Soc.* **2000**, *122*, 5695–5709.
9. Peymann, T.; Knobler, C. B.; Khan, S. I.; Hawthorne, M. F. Dodecahydroxy-*closo*-dodecaborate(2−). *J. Am. Chem. Soc.* **2001**, *123*, 2182–2185.
10. Farha, O. K.; Julius, R. L.; Lee, M. W.; Huertas, R. E.; Knobler, C. B.; Hawthorne, M. F. Synthesis of Stable Dodecaalkoxy Derivatives of *hypercloso*-$B_{12}H_{12}$. *J. Am. Chem. Soc.* **2005**, *127*, 18243–18251.
11. Voronkov, M. G.; Lavrent'yev, V. I. Polyhedral Oligosilsesquioxanes and Their Homo Derivatives. *Top. Curr. Chem.* **1982**, *102*, 199–236.
12. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. Silsesquioxanes. *Chem. Rev.* **1995**, *95*, 1409–1430.
13. Provatas, A.; Matisons, J. G. Synthesis and Applications of Silsesquioxanes. *Trends Polym. Sci.* **1997**, *5*, 327–333.
14. Loy, D. A.; Shea, K. J. Bridged Polysilsesquioxanes. Highly Porous Hybrid Organic−Inorganic Materials. *Chem. Rev.* **1995**, *95*, 1431–1442.
15. Laine, R. M. Nanobuilding blocks based on the $[OSiO_{1.5}]_x$ (x = 6, 8, 10) silsesquioxanes. *J. Mater. Chem.* **2005**, *15*, 3725–3744.
16. Lichtenhan, J. D.; Vu, H. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. Silsesquioxane−Siloxane Copolymers from Polyhedral Silsesquioxanes. *Macromolecules* **1993**, *26*, 2141–2142.
17. Gilman, J. W.; Schlitzer, D. S.; Lichtenhan, J. D. Low Earth Orbit Resistant Siloxane Copolymers. *J. Appl. Polym. Sci.* **1996**, *60*, 591–596.
18. Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. In Situ Oxygen-Atom Erosion Study of Polyhedral Oligomeric Silsesquioxane−Siloxane Copolymer. *J. Spacecraft Rockets* **2000**, *37*, 463–467.
19. Weidner, R.; Zeller, N.; Deubzer, B.; Frey, V. Organooligosilsesquioxanes. U.S. Patent 5,047,492, Sept 1990.
20. Hoebbel, D.; Pitsch, I.; Hiller, W.; Dathe, S.; Popowski, E.; Sonnek, G.; Reiher, T.; Jancke, H.; Scheim, U. Eur. Patent 348,705 A2, 1990.
21. Freyer, C.; Wolferseder, J.; Peetz, U. Eur. Patent 624591 A1, 1994.
22. Zhang, Y.; Lee, S. H.; Yoonessi, M.; Liang, K.; H.; Pittman, C. U., Jr. Phenolic Resin− Trisilanolphenyl Polyhedral Oligomeric Silsesquioxane (POSS) Hybrid Nanocomposites: Morphology and Structure. *Polymer* **2006**, *47*, 2984–2996.
23. Patel, R. R.; Mohanraj, R.; Pittman, C. U., Jr. Properties of Polystyrene and Polymethyl Methacrylate Copolymers of Polyhedral Oligomeric Silsesquioxanes: A Molecular Dynamics Study. *J. Polym. Sci. B: Polym. Phys.* **2006**, *44*, 234–248.
24. Liang, K.; Li, G. Z.; Toghiani, H.; Koo, J. H.; Pittman, C. U., Jr. Cyanate Ester/Polyhedral Oligomeric Silsesquioxane (POSS) Nanocomposites: Synthesis and Characterization. *Chem. Mater.* **2006**, *18*, 301–312.
25. Stewart, M. D.; Willson, C. G. Imprint Materials for Nanoscale Devices. *MRS Bull.* **2005**, *30*, 947–951.
26. Stewart, M. D.; Wetzel, J. T.; Schmid, G. M.; Palmieri, F.; Thompson, E.; Kim, E. K.; Wang, D. D.; Sotodoeh, K.; Jen, K.; Johnson, S. C.; *et al.* Direct Imprinting of Dielectric Materials for Dual Damascene Processing. *Proc. SPIE−Int. Soc. Opt. Eng.* **2005**, *5751*, 210–218.
27. Hasegawa, I.; Sakka, S.; Sugahara, Y.; Kuroda, K.; Kato, C. Silicate Anions Formed in Tetramethylammonium Silicate Methanolic Solutions as Studied by ^{29}Si Nuclear Magnetic Resonance. *J. Chem. Soc., Chem. Commun.* **1989**, 208–210.
28. Hasegawa, I.; Sakka, S. Rapid Solidification of (2-hydroxyethyl)trimethylammonium silicate. *Chem. Lett.* **1988**, 1319–1322.
29. Agaskar, P. A. New Synthetic Route to the Hydriospherosiloxanes O_h-$H_8Si_8O_{12}$ and D_{5h} -$H_{10}Si_{10}O_{15}$. *Inorg. Chem.* **1991**, *30*, 2707–2708.
30. Hoebbel, D.; Endres, K.; Reinert, T.; Pitsch, I. Inorganic-organic polymers derived from functional silicic acid derivatives by additive reaction. *J. Non-Cryst. Solids* **1994**, *176*, 179–188.
31. Hoebbel, D.; Pitsch, I.; Heidmann, D. Inorganic Organic Polymers with Defined Silicic Acid Units. In *Eurogel '91*; Proceedings of the Second European Conference on Sol-Gel Technology; Elsevier Science Publishers: Amsterdam, 1992; pp 467–473..

32. Hong, B.; Thoms, T. P. S.; Murfee, H. J.; Lebrun, M. J. Highly Branched Dendritic Macromolecules with Core Polyhedral Silsesquoxane Functionalities. *Inorg. Chem.* **1997**, *36*, 6146–6147.
33. Feher, F. J.; Wyndham, K. D. Amine and ester-substituted silsesquioxanes; synthesis, characterization and use as a core for starburst dendrimers. *Chem. Commun.* **1998**, 323–324.
34. Dvornic, P. R.; Hartmann-Thompson, C.; Keinath, S. E.; Hill, E. J. Organic−Inorganic Polyamidoamine (PAMAM) Dendrimer−Polyhedral Oligosilsesquoixane (POSS) Nanohybrids. *Macromolecules* **2004**, *37*, 7818–7831.
35. Kim, G.-M.; Qin, H.; Fang, X.; Sun, F. C.; Mather, P. T. Hybrid Epoxy-Based Thermosets Based on Polyhedral Oligosilsesquioxanes: Cure Behavior and Toughening Mechanisms. *J. Polym. Sci. B: Polym. Phys.* **2003**, *41*, 3299–3313.
36. Kim, B.-S.; Mather, P. T. Amphiphilic Telechelics Incorporating Polyhedral Oligosilsesquioxane: 1. Synthesis and Characterization. *Macromolecules* **2002**, *35*, 8378–8384.
37. Waddon, A. J.; Coughlin, E. B. Crystal Structure of Polyhedral Oligomeric Silsesquioxane (POSS) Nano-materials: A Study by X-ray Diffraction and Electron Microscopy. *Chem. Mater.* **2003**, *15*, 4555–4561.
38. Cardoen, G.; Coughlin, E. B. Hemi-Telechelic Polystyrene−POSS Copolymers as Model Systems for the Study of Well-Defined Inorganic/Organic Hybrid Materials. *Macromolecules* **2004**, *37*, 5123–5126.
39. Fu, B. X.; Hsiao, B. S.; White, H.; Rafailovich, M.; Mather, P.; Joen, H. G.; Phillips, S.; Lichtenhan, J.; Schwab, J. Nanoscale Reinforcement of Polyhedral Oligomeric Silsesquioxane (POSS) in Polyurethane Elastomer. *Polym. Int.* **2000**, *49*, 437–440.
40. Fu, B. X.; Zhang, W.; Hsiao, B. S.; Rafailovich, M.; Sokolov, J.; Johansson, G.; Sauer, B. B.; Phillips, S.; Blanski, R. Synthesis and Characterization of Segmented Polyurethane Containing Polyhedral Oligomeric Silsesquioxane (POSS) Nanostructured Molecules. *High Performance Polym.* **2000**, *12*, 565–571.
41. Lin, H.-C.; Kuo, S.-W.; Huang, C.-F.; Chang, F.-C. Thermal and Surface Properties of Phenolic Nanocomposites Containing Octaphenol Polyhedral Oligomeric Silsesquioxane. *Macromol. Rapid Commun.* **2006**, *27*, 537–541.
42. Baker, E. S.; Gidden, J.; Anderson, S. E.; Haddad, T. S.; Bowers, M. T. Isomeric Structural Characterization of Polyhedral Oligomeric Silsesquioxanes (POSS) with Styryl and Epoxy Phenyl Capping Agents. *Nano Lett.* **2004**, *4*, 779–785.
43. Fu, B. X.; Lee, A.; Haddad, T. S. Styrene−Butadiene−Styrene Triblock Copolymers Modified with Polyhedral Oligomeric Silsesquioxanes. *Macromolecules* **2004**, *37*, 5211–5218.
44. Kopesky, E. T.; Haddad, T. S.; Cohen, R. E.; McKinley, G. H. Thermomechanical Properties of Poly(methyl methacrylate)s Containing Tethered and Untethered Polyhedral Oligomeric Silsesquioxanes. *Macromolecules* **2004**, *37*, 8992–9004.
45. Sellinger, A.; Laine, R. M. Silsesquioxanes as Synthetic Platforms. Thermally and Photo Curable Inorganic/Organic Hybrids. *Macromolecules* **1996**, *29*, 2327–2330.
46. Choi, J.; Harcup, J.; Yee, A. F.; Zhu, Q.; Laine, R. M. Organic/Inorganic Hybrid Composites from Cubic Silsesquioxanes. *J. Am. Chem. Soc.* **2001**, *123*, 11420–11430.
47. Laine, R. M.; Choi, J.; Lee, I. Organic-Inorganic Nanocomposites with Completely Defined Interfacial Interactions. *Adv. Mater.* **2001**, *13*, 800–803.
48. Tamaki, R.; Tanaka, Y.; Asuncion, M. Z.; Choi, J.; Laine, R. M. Octa(aminophenyl)sil-sesquioxane as a Nanoconstruction Site. *J. Am. Chem. Soc.* **2001**, *123*, 12416–12417.
49. Tamaki, R.; Choi, J.; Laine, R. M. A Polyimide Nanocomposite from Octa(aminophenyl)silsesquioxane. *Chem. Mater.* **2003**, *15*, 793–797.
50. Choi, J.; Tamaki, R.; Kim, S. G.; Laine, R. M. Organic/Inorganic Imide Nanocomposites from Aminophenylsilsesquioxanes. *Chem. Mater.* **2003**, *15*, 3365–3375.
51. Choi, J.; Yee, A. F.; Laine, R. M. Organic/Inorganic Hybrid Composites from Cubic Silsesquioxanes. Epoxy Resins of Octa(dimethylsiloxyethylcyclohexylepoxide) Silsesquioxane. *Macromolecules* **2003**, *36*, 5666–5682.
52. Brick, C. M.; Ouchi, Y.; Chujo, Y.; Laine, R. M. Robust Polyaromatic Octasilsesquioxanes from Polybromophenylsilsesquioxanes, Br$_x$OPS, via Suzuki Coupling. *Macromolecules* **2005**, *38*, 4661–4665.
53. Zhang, Z. L.; Horsch, M. A.; Lamm, M. H.; Glotzer, S. C. Tethered Nano Building Blocks: Toward a Conceptual Framework for Nanoparticle Self-Assembly. *Nano Lett.* **2003**, *3*, 1341–1343.
54. Neumann, D.; Fisher, M.; Tran, L.; Matisons, J. G. Synthesis and Characterization of an Isocyanate Functionalized Polyhedral Oligosilsesquioxane and the Subsequent Formation of an Organic−Inorganic Hybrid Polyurethane. *J. Am. Chem. Soc.* **2002**, *124*, 13998–13999.
55. Maitra, P.; Wunder, S. L. Oligomeric Poly(ethylene oxide)-Functionalized Silsesquioxanes: Interfacial Effects on T_g, T_m, and H_m. *Chem. Mater.* **2002**, *14*, 4494–4497.
56. Mehl, G. H.; Goodby, J. W. Liquid-Crystalline, Substituted Octakis(dimethylsiloxy)octasilsesquioxane: Oligomeric Supramolecular Materials with Defined Topology. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2641–2643.
57. Takahashi, K.; Sulaiman, S.; Katzenstein, J. M.; Snoblen, S.; Laine, R. M. New Aminophenylsilsesquioxanes, Synthesis, Properties and Epoxy Nanocomposites. *Aust. J. Chem.* **2006**, *59*, 564–570.
58. Sulaiman, S.; Brick, C. M.; De Sana, C. M.; Katzenstein, J. M.; Laine, R. M.; Basheer, R. A. Tailoring the Global Properties of Nanocomposites. Epoxy Resins with Very Low Coefficients of Thermal Expansion. *Macromolecules* **2006**, *39*, 5167–5169.
59. Asuncion, M. Z.; Laine, R. M. Silsesquioxane Barrier Materials. *Macromolecules* **2007**, *40*, 555–562.
60. Brick, C. M.; Chan, E. R.; Glotzer, S. C.; Martin, D. C.; Marchal, J. C.; Laine, R. M. Self-lubricating nano ball bearings. *Adv. Mater.* **2007**, *19*, 82–89.
61. Feher, F. J.; Budzichowski, T. A. Syntheses of highly-functionalized polyhedral oligosilsesquioxanes. *J. Organomet. Chem.* **1989**, *379*, 33–40.
62. Sellinger, A.; Tamaki, R.; Laine, R. M.; Ueno, K.; Tanabe, H.; Williams, E.; Jabbour, G. E. Heck Coupling of Haloaromatics with Octavinylsilsesquioxane: Solution Processable Nanocomposites for Application in Electroluminescent Devices. *Chem. Commun.* **2005**, 3700–3702.
63. Lo, M. Y.; Zhen, C.; Lauters, M.; Jabbour, G. E.; Sellinger, A. Organic−Inorganic Hybrids Based on Pyrene Functionalized Octavinylsilsesquioxanes Cores for Applications in OLEDS. *J. Am. Chem. Soc.* **2007**, *129*, 5808–5809.
64. Marciniec, B.; Pietraszuk, C. Synthesis of Unsaturated Organosilicon Compounds Via Alkene Methathesis and Metathesis Polymerization. *Curr. Org. Chem.* **2003**, *7*, 691–735.
65. Kujawa-Welten, M.; Pietraszuk, C.; Marciniec, B. Cross-Metathesis of Vinylsilanes with Allyl Alkyl Ethers Catalyzed by Ruthenium−Carbene Complexes. *Organometallics* **2002**, *21*, 840–845.
66. Stang, P. J.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 1988.
67. Frost, C. G.; Mendonca, P. Recent Developments in Heteroatom Coupling Reactions. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2616–2623.
68. Asuncion, M. Z.; Laine, R. M. Acetylene Stars from [*p*-I-PhSiO$_{1.5}$]$_8$. *Macromolecules*,manuscript submitted.
69. Tamao, K.; Ishida, N.; Kumada, M. (Diisopropoxymethylsilyl)methyl Grignard Reagent: A New, Practically Useful Nucleophilic Hydroxymethylating Agent. *J. Org. Chem.* **1983**, *48*, 2120–2122.

70. Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. Silafunctional Compounds in Organic Synthesis. Part 20. Hydrogen Peroxide Oxidation of the Silicon−carbon Bond in Organoalkoxysilanes. *Organometallics* **1983**, *2*, 1694–1696.
71. Fleming, I.; Sanderson, P. E. J. A one-pot conversion of the phenyldimethylsilyl group into a hydroxyl group. *Tetrahedron Lett.* **1987**, *28*, 4229–4232.
72. The carbazole and nitrile compounds are not amenable to this cleavage technique, likely because of oxidation of the nitrogens.
73. Vogel, A. I. Purification of solid organic compounds by recrystallization. General considerations. *Practical Organic Chemistry*; John Wiley & Sons: New York, 1966; pp 122–125..
74. Croswell, R. T.; Reisman, A.; Simpson, D. L.; Temple, D.; Williams, C. K. Differential Thermal Analysis of Glass Mixtures Containing SiO_2, GeO_2, B_2O_3, and P_2O_5. *J. Electrochem. Soc.* **1999**, *146*, 4569–4579.
75. See, for example: Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. Exceptional H_2 Saturation Uptake in Microporous Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2006**, *128*, 3494–3495.
76. Evans, R. C.; Douglas, P.; Winscom, C. J. Coordination Complexes Exhibiting Room-Temperature Phosphorescence: Evaluation of their Suitability as Triplet Emitters in Organic Light Emitting Diodes. *Coord. Chem. Rev.* **2006**, *250*, 2093–2126, and references therein.
77. Hung, L. S.; Chen, C. H. Recent progress of molecular organic electroluminescent materials and devices. *Mater. Sci. Eng., R* **2002**, *39*, 143–222.
78. Mitschke, U.; Bäuerle, P. The electroluminescence of organic materials. *J. Mater. Chem.* **2000**, *10*, 1471–1507.
79. Jenekhe, S. A. The Special Issue on Organic Electronics. *Chem. Mater.* **2004**, *16*, 4381–4382.
80. Brown, J. F.; Vogt, L. H.; Prescott, P. I. Preparation and Characterization of the Lower Equilibrated Phenylsilsesquioxanes. *J. Am. Chem. Soc.* **1964**, *86*, 1120–1124.
81. Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerrner, R. S.; Cai, D.; Larsen, R. D.; Reider, P. J. An Improved Protocol for the Preparation of 3-Pyridyl- and Some Arylboronic Acids. *J. Org. Chem.* **2002**, *67*, 5394–5397.
82. Babudri, F.; Farinola, G. M.; Naso, F. Synthesis of conjugated oligomers and polymers: the organometallic way. *J. Mater. Chem.* **2004**, *14*, 11–34.
83. Kimoto, A. C.; Cho, J. S.; Higuchi, M. Synthesis of Asymmetrically Arranged Dendrimers with a Carbazole Dendron and a Phenylazomethine Dendron. *Macromolecules* **2004**, *37*, 5531–5537.
84. Balthazor, T. M.; Grabiak, R. C. Nickel-Catalyzed Arbuzov Reaction: Mechanistic Observations. *J. Org. Chem.* **1980**, *45*, 5425–5426.
85. Negishi, E.; Anastasia, L. Palladium-Catalyzed Alkynylation. *Chem. Rev.* **2003**, *103*, 1979–2017.