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Crystalline Hybrid Polyphenylene Macromolecules from Octaalkynylsilsesquioxanes, Crystal Structures, and a Potential Route to 3-D Graphenes

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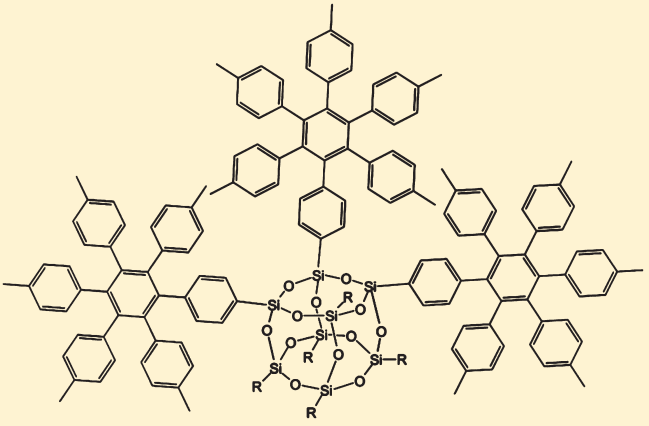
Supporting Information

ABSTRACT: We report here the Diels–Alder reaction of octa(diphenylacetylene)silsesquioxane [DPA_8OS] with tetraphenylcyclopentadienone or tetra(*p*-tolyl)cyclopentadienone to form octa(hexaphenylbenzene)octasilsesquioxane, $(Ph_6C_6)_8OS$, or octa(tetratolyldiphenylbenzene)octasilsesquioxane, $(p\text{-Tolyl}_4\text{-}Ph_2C_6)_8OS$. Likewise, tetra(*p*-tolyl)cyclopentadienone reacts with octa(*p*-tolylethynylphenyl)OS to form octa(pentatolylphenylbenzene)octasilsesquioxane $(p\text{-Tolyl}_5PhC_6)_8OS$. These compounds, with molecular weights of 4685–5245 Da, were isolated and characterized using a variety of analytical methods. The crystal structure of DPA_8OS offers a 3 nm^3 unit cell with $Z = 1$. The crystal structure of $(Ph_6C_6)_8OS$ was determined to have a triclinic unit cell of 11 nm^3 with $Z = 1$. The latter structure is believed to be the largest discrete molecular structure reported with 330 carbons. Efforts to dehydrogenatively cyclize (Scholl reaction) the hexaarylbenzene groups to form 3-D octgraphene compounds are described.



INTRODUCTION

The unique properties and symmetries of polyhedral silsesquioxanes offer considerable potential as novel materials in their own right but also offer potential for use as 3-D modular, synthetically flexible nanobuilding blocks (NBs)[1−3] for the design and synthesis (assembly) of 3-D nanostructured materials.[1−5] Many groups have embraced the idea of using nanobuilding blocks based on cubanes[6a] dodecahedral boranes[6b] or secondary building units[6c] to develop tailored materials; however, these NBs tend to be costly and synthetically intensive.[6] Alternately, cubic octasilsesquioxanes (OSs) as depicted in Figure 1 offer perfect 3-D symmetry with average diameters of 1 nm. Because they are easily synthesized, purified, and functionalized with diverse reactive moieties, OSs offer great potential to design, structure precise, tailorable NBs.

To this end, we recently demonstrated routes to pure ortho-brominated and para-iodinated phenylsilsesquioxanes: $[o\text{-Br-PhSiO}_{1.5}]_8$[4] and $[p\text{-I-PhSiO}_{1.5}]_8$[5] cubic silsesquioxane NBs. Both compounds are easily functionalized using traditional cross-coupling reactions. Furthermore, most recently we demonstrated that $[p\text{-I-PhSiO}_{1.5}]_8$ on heating to ≥425 °C loses I_2 forming novel crystalline, 3-D microporous materials that are air-stable to >500 °C and appear to retain their original crystal packing structures.[5b]

We have also demonstrated multiple methods of functionalizing $[PhSiO_{1.5}]_8$ to produce highly symmetrical compounds with additional functionality.[4−20] In particular, we find that the octaalkynylOS compounds serve as versatile starting points for further elaboration including the synthesis of a second set of microporous 3-D structures.[5b−d] We report here their use in building much larger 3-D macromolecular structures through the use of traditional Diels–Alder methods with the goal of exploring their utility as components in 3-D organic electronic applications.[21−23]

Research in the area of organic electronics has received intense recent interest as these materials offer potential as components in low-cost, high-quality display applications (e.g., OLEDs) and for

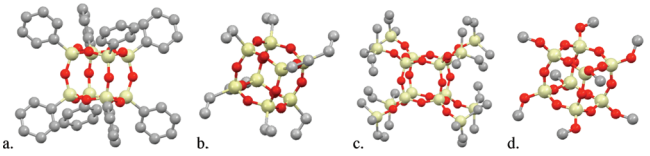


Figure 1. (a) OctaphenylOS ($C_{48}H_{40}Si_8O_{12}$), (b) octavinylOS ($C_{16}H_{24}Si_8O_{12}$), (c) octa(vinyldimethylsiloxy)OS ($Si_{16}O_{20}C_{32}H_{72}$), and (d) octamethoxyOS ($Si_8O_{20}C_8H_{24}$).

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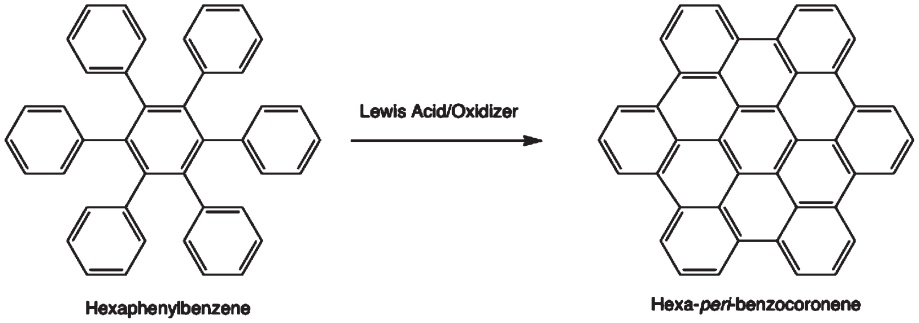
Scheme 1. Scholl Cyclization of Hexaphenylbenzene (HPB) to Hexa-*peri*-benzocoronene (HBC)



organic/hybrid photovoltaics. In part, this interest derives from the ease with which it is possible to tailor aromatic substituted OSs to modify band gaps, tune processing properties, and employ lower cost processing methods.[26,27]

The utility of conjugated organic polymers such as polyphenylenevinylenes, polyphenyleneethynylenes, and polyarylenes in such applications has been reviewed by others;[21−32] here we describe efforts to develop OS hybrids starting as possible supplements or replacements for wholly organic materials.[33] Chan et al. recently reviewed the use of OS-based materials in this capacity, describing enhancements in performance, solid-state morphology, and stability.[33]

Our goal is to provide 3-D alternatives to the well-established 2-D compounds currently in use for organic electronic applications. In part, our efforts are motivated by the fact that SQs with attached moieties "conjugated" with the cage seem to exhibit 3-D electronic/photonic interactions in the excited state through the cage itself.[27] These interactions include exceptional increases in two-photon absorption cross sections and extensive red shifts in emission relative to the emissions from the organic moiety itself.[27]

The potential to introduce 3-D semiconducing components could change the structures one might use in both OLED and photovoltaic applications. Both hole and electron transport might be anticipated to change as well as absorption and emission efficiencies, as we have shown previously.[34]

A number of groups, especially that of Müllen, have recognized that Diels−Alder condensation of alkynes with dienones offers an efficient and facile route for the synthesis of polyarylbenzenes and very large polyphenylene systems.[32] Pascal et al. explored polyphenylenes consisting of nearly 300 carbon atoms and determined their crystal structures.[37−41] Müllen et al. used this chemistry to divergently synthesize polyphenylene dendrimers with molecular weights greater than 1 million Da.[42−45]

Carbon allotropes are of perennial interest, and the latest trend is the synthesis and modification of graphenes.[21] The planar configuration allows for extensive π-electron delocalization, giving rise to electronic[22] and magnetic[23] properties of great interest for advanced integrated circuits.[54−56] Hexaarylbenzenes further serve as precursors for the synthesis of planar graphene-like or polynuclear aromatic hydrocarbon (PAH) compounds via intramolecular dehydrogenative cyclization (Scholl reaction).[46] In the case of hexaphenylbenzene, Scholl cyclization gives the planar hexa-*peri*-benzocoronene, studied in great detail by Müllen et al. (Scheme 1).[45−48]

The Scholl reaction has been studied extensively experimentally[34−36,46−48,56−63] and, more recently, theoretically.[56,57] Early work conducted by Kovacic et al. investigated $AlCl_3$-catalyzed polymerization of benzene using cupric or ferric chlorides as oxidants and the latter as an alternate catalyst.[35,36] Kovacic et al. found that protons are stripped from para positions, and new carbon−carbon bonds form between two adjacent phenyl groups.[34]

Computational analysis suggests that HPB reacts rapidly and intramolecularly to form hexa-*peri*-benzocoronene (HBC),[57,58] though in some instances Müllen et al. were able to isolate partially cyclized hexaarylbenzenes.[46,57,58] Lewis acids and oxidants including $AlCl_3/CuCl_2$, $FeCl_3$, $MoCl_5$, $VOCl_3$, and DDQ/protic acid have all been used for the same purpose.[28,34−36,46−48,56−63]

Our discovery of routes to perfectly symmetrical octaalkynes from $[p\text{-IPhSiO}_{1.5}]_8$ per Scheme 2 provides the impetus to synthesize a wide variety of octahexarylbenzenes and thereafter cyclize them via the Scholl reaction per Scheme 3. Our overall goal has been to synthesize *octagraphenes*, cubic OSs with a periphery of eight hexa-*peri*-benzocoronene moieties.

Below we detail our efforts to develop high-yield, high-conversion Diels−Alder reactions of selected octaalkynes with tetraphenylcyclopentadienone and tetra-*p*-tolylcyclopentadienone, and thereafter their Scholl cyclization using $FeCl_3/CH_3NO_2$.

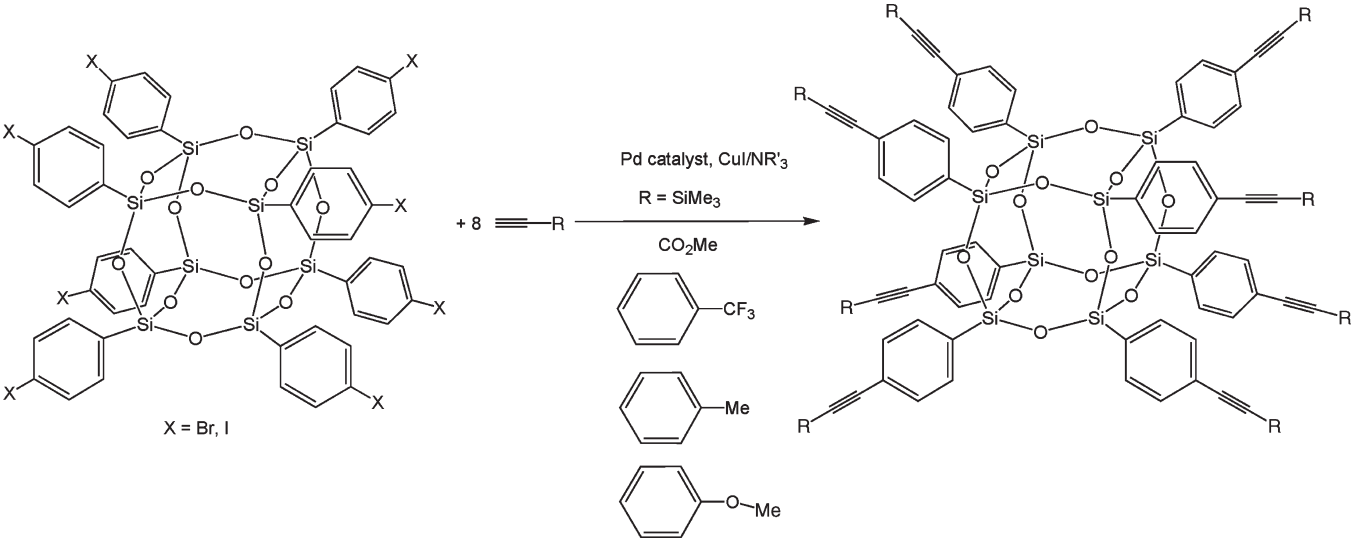
EXPERIMENTAL SECTION

Materials. *N*-Methyldicylohexylamine, tri-*o*-tolylphosphine, phenylacetylene, ethynyltoluene, tetraphenylcyclopentadienone, and other synthetic reagents were purchased from Sigma-Aldrich and used as received. Pd_2dba_3 and bis(tri-*tert*-butylphosphine)palladium(0) were purchased from Strem Chemicals. Solvents were dried over 4 Å molecular sieves. Dioxane and THF were distilled from sodium benzophenone ketyl under nitrogen. I_8OPS was synthesized as previously described[5a] and recrystallized twice from 50:50 ethyl acetate:toluene to reach purity >95%.[5a,b]

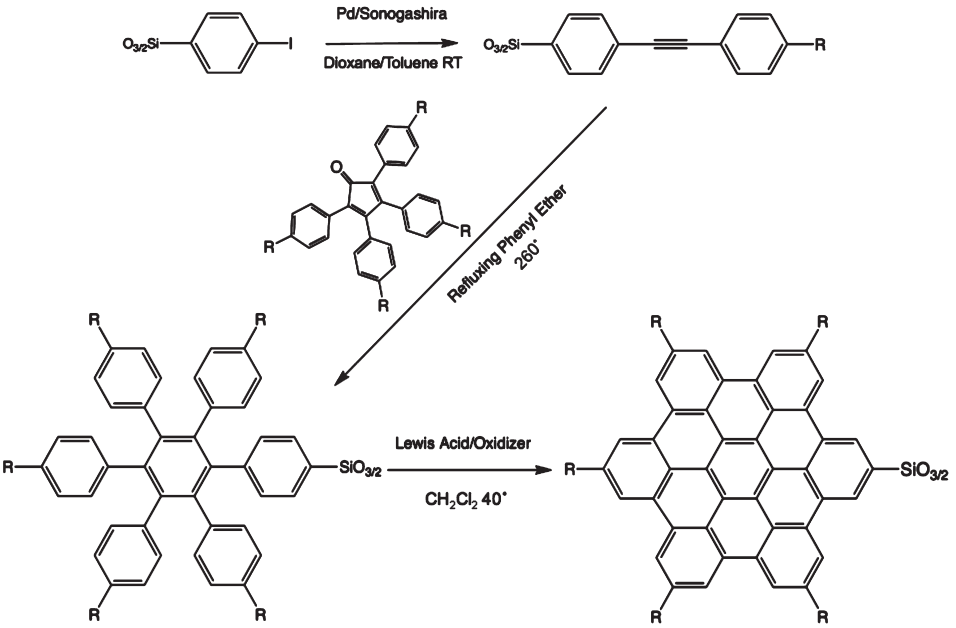
Analytical Methods. *Nuclear Magnetic Resonance (NMR).* All ^1H NMR spectra were collected from samples dissolved in $CDCl_3$ and recorded on a Varian INOVA 400 MHz spectrometer. ^1H spectra were collected at 400 MHz using a 6000 Hz spectral width, a relaxation delay of 3.5 s, 30K data points, a pulse width of 38°, and $CHCl_3$ (7.24 ppm) as the internal reference. ^{13}C spectra were collected at 100 MHz using 25141.4 Hz spectral width, a relaxation delay of 0.1 s, a 45° pulse width with 256 repetitions, and $CHCl_3$ (77.23 ppm) as the internal reference.

Thermogravimetric Analyses (TGA/DTA). All TGA/DTA analyses were run on a 2960 simultaneous DTA-TGA Instrument (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.

Scheme 2. Synthesis of OctaalkynylOSs from $[p\text{-IPhSiO}_{1.5}]_8$[64,65]



Scheme 3. Proposed General Synthesis of Octagraphenes



Matrix-Assisted Laser Desorption/Time-of-Flight Spectrometry. (MALDI-TOF) was done on a Micromass TofSpec-2E 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), and optionally 1 part $AgNO_3$ (2.5 mg/mL in water) and blotting the mixture on the target plate.

The resulting chromatograms were averaged and smoothed once using the Savitzky−Golay algorithm. The baseline was subtracted using a 99th-order polynomial, and the spectra were centered using a channel width of half the full width at half-maximum.

General Sonogashira Coupling Reaction. To a dry 50 mL Schlenk flask under N_2 and equipped with a magnetic stir bar under was added 4 g of I_8OPS (16 mmol of aryl iodide), tris(triphenylphosphine)CuI, 10 mg (0.168 mmol, 7%) of bis(tri-*tert*-butylphosphine) palladium(0), and 9 mg of tris(benzylideneacetone)dipalladium(0). Subsequently 12 mL of toluene (previously distilled and degassed), 2 mL (2.6 mmol) of phenylacetylene, and 3.6 mL of *N*-methyldicyclohexylamine were added to the flask while stirring followed by 12 mL of 1,4-dioxane (previously distilled and degassed). The solution was stirred at RT for 48 h. The solution turned yellow-brown. The mixture precipitated into ~100 mL of methanol to deactivate the catalyst. The resulting precipitate was collected by filtration. The dried precipitate was partially dissolved in ~10 mL of toluene, and tetrahydrofuran was added until the solution was clear and homogeneous. A tetrahydrofuran solution of *n*-acetyl-L-cysteine was added along with 1 g each of Celite and activated carbon. The suspension was briefly stirred and allowed to

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sit overnight. After 24 h the suspension was filtered and precipitated to yield a yellow powder, which could be recrystallized from hot *m*-xylene to yield 410 mg of off-white crystals (~10% of theoretical for complete conversion). The amorphous material was precipitated into cold methanol to give 2.25 g of yellow powder. Total yield: 67% of theoretical for complete conversion.

Octa(4-methyldiphenylacetylene)silsesquioxane: yield 92% of theoretical for complete conversion. Recrystallization from *m*-xylene gave 270 mg as off-white crystals; 14% of theoretical for complete conversion.

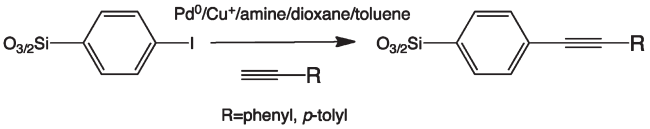
Tetra-*p*-tolylcyclopentadienone. In a 250 mL flask were put 13.5 g (90 mmol) of tolylacetic acid and 3.3 g (27 mmol) of DMAP in 30 mL of dry methylene chloride. Stirring was started, and a solution of 10.7 g (52 mmol) of DCC in 55 mL of dry methylene chloride was added. Evolution of CO_2 was seen, and the solution turned orange. Stirring was continued overnight. 150 mL of 50:50 hexane ethyl acetate was added, and the organic layer was extracted over a pH 4 potassium biphthalate buffer solution to remove DMAP, then a saturated sodium bicarbonate solution to remove residual tolylacetic acid, and finally with brine. The organic layer was filtered and rotovaped to an oil and placed in the freezer to crystallize. Crystals were isolated by filtration and washing with a small portion ~30 mL of hexane and dried under vacuum, yielding 9.5 g (40 mmol, ~88% of theoretical). The crystals were dissolved into ethanol with 9.5 g (40 mmol) of dimethylbenzil and heated in 75 mL of hot ethanol. The mixture was heated to boiling, and 1.2 g of KOH in 10 mL of ethanol was added by pipet. The dark mixture was refluxed for 15 min and then cooled with ice. The dark blue/black crystalline tetracyclone was isolated by filtration and washed with methanol, methanol/water, and methanol. The crystals were dried, redispersed in methanol, filtered, and washed with methanol, methanol/water, and methanol. The total yield of crystals was 12.4 g (70% of theoretical), shown to be pure via ^{1}H NMR (see Supporting Information).

$(Ph_6C_6)_8OS$. To a dry 20 mL round-bottom flask was added 0.45 g (2 mmol) of recrystallized octadiphenylacetylene followed by the addition of tetraphenylcyclopentadienone (0.75 g, 2 mmol). Diphenyl ether, ~5 mL, was added by pipet, and a condenser was attached. After introducing a slow nitrogen flow, the dark purple solution was heated to reflux and stirred for 2 days. At this time, the flask was loosely capped and allowed to cool to room temperature. During cooling product crystallized out over a 1 day period. The mixture was diluted by addition of ~10 mL of ethyl acetate and filtered to yield fine tan crystals. The filtrate was precipitated into ~100 mL of cold methanol to yield a tan powder. While the total isolated yield is essentially quantitative, serial recrystallization provided 0.4 g of highly crystalline octa(hexaphenylbenzene) octasilsesquioxane (35% of theoretical for complete conversion). Single crystals suitable for X-ray diffraction were grown from hot toluene.

(p-Tolyl$_5$PhC_6)$_8$OS. To a dry 20 mL round-bottom flask was added 200 mg of recrystallized tolylethynylphenylsilsesquioxane followed by the addition of tetratolylcyclopentadienone (363 mg). Diphenyl ether, ~5 mL, was added by pipet, and a condenser was attached. After introducing a slow nitrogen flow, the dark purple solution was heated to reflux and stirred for 1 day. After cooling to room temperature, 10 mL of ethyl acetate was added, and the solution was precipitated into ~100 mL of cold methanol, giving a tan powder. This powder was redissolved into 10 mL of ethyl acetate and precipitated into 100 mL of cold methanol. The precipitate was collected by filtration, giving 408 mg of tan powder (75% of theoretical yield). The product was very soluble in toluene, ethyl acetate, xylenes, and tetrahydrofuran. Recrystallization of the product could be accomplished by dissolution in a minimum of hot toluene, followed by the addition of 10−20 volumes of acetone, and placing the solution in a freezer for several days.

(p-Tolyl$_4$Ph$_2C_6$)$_8$OS. To a dry 20 mL round-bottom flask was added 200 mg of recrystallized octadiphenylacetylenelsilsesquioxane followed by the addition of tetratolylcyclopentadienone (370 mg). Diphenyl ether, ~5 mL, was added by pipet, and a condenser was attached. After introducing a slow nitrogen flow, the dark purple solution was heated to reflux and stirred for 1 day. After cooling to room temperature, 10 mL of ethyl acetate was added, and the solution precipitated into ~100 mL of cold methanol, giving a tan powder. This powder was redissolved into 10 mL of ethyl acetate and precipitated into 100 mL of cold methanol. The precipitate was collected by filtration, giving 376 mg of tan powder (64% of theoretical yield). Recrystallization from nitrobenzene gave 60 mg of pale yellow crystals. Single crystals suitable for X-ray diffraction were grown from hot *m*-xylene/tetradecane.

Scheme 4. Sonogashira Coupling of Terminal Acetylene and Iodophenylsilsesquioxane



RESULTS AND DISCUSSION

The first step in our efforts to develop 3-D graphene systems using octa-alkyne SQs involved the optimization of the Songashira coupling process.

Sonogashira Coupling. Sonogashira coupling (Scheme 4) optimization studies were undertaken to ensure that the yield of fully octa-substituted alkynes would be >99%. The Pd(*t*-Bu$_3$P)$_2$/Pd$_2$DBA$_3$ cocatalyst was described previously;[5c] however, the CuI cocatalyst was replaced with CuI(PPh$_3$)$_3$[5d,66] to improve reaction homogeneity. The reaction is conducted preferably at RT, but low catalyst activity may require heating to 40−60 °C. Reaction progress was monitored by MALDI-TOF (Table 1) of aliquots precipitated into cold methanol.

On completion, the reaction mixture was precipitated into cold methanol and filtered. The crude material was redissolved in toluene and treated with THF solutions of *N*-acetyl-L-cysteine to remove residual palladium.[67] After sitting overnight at room temperature, the suspension was filtered and reprecipitated into cold methanol. Single crystals suitable for X-ray diffraction were obtained by slowly cooling hot, saturated *m*-xylene or ethyl acetate solutions of the octaalkynes.

The NMR data for derivatives **1a** and **1b** are detailed in the Supporting Information (Figures S.1−S.2, S.4−S.5) with the benzylic protons representing 28% of the total integration (27.3% expected). The results may be summarized by saying that, based on NMR spectra modeling,[68] the SQ cage exhibits electron-withdrawing character lying between CF_3 and NO_2. MALDI-TOF MS data are also provided in the Supporting Information (Figures S.3, S.6), showing the high purity of the octaisomer, **1a**. The mass spectrum for **1b** shows small amounts of hepta- and nona-substituted species; however, these peaks are small, and the presumed differences in ionization potential preclude a quantitative analysis.

Single-crystal X-ray diffraction analysis indicates that **1a** crystallizes in the triclinic space group *P*-1 (Figure 2). The structure was refined to an *R*-factor of 5.5%. Additional crystallographic details are provided in Table 2.

Diels−Alder Condensation with Tetraarylcyclopentadienones. Diels−Alder condensation of diphenylacetylene with tetraphenylcyclopentadienone (tetracyclone) giving hexaphenylbenzene

Table 1. Characterization of Ethynyl Derivatives

sample	yield (%)	MW calculated (Ag^+ ion)	MW MALDI-TOF found (% intensity)	ceramic yield (%) (theory)	ceramic yield (%) (found)
DPA_8OS (**1a**)	67	1942.35	1941.7 (100)	26	25
(p-tolylethynylphenyl)$_8$OS (**1b**)	91	2054.57	2053.7 (100)	23	23

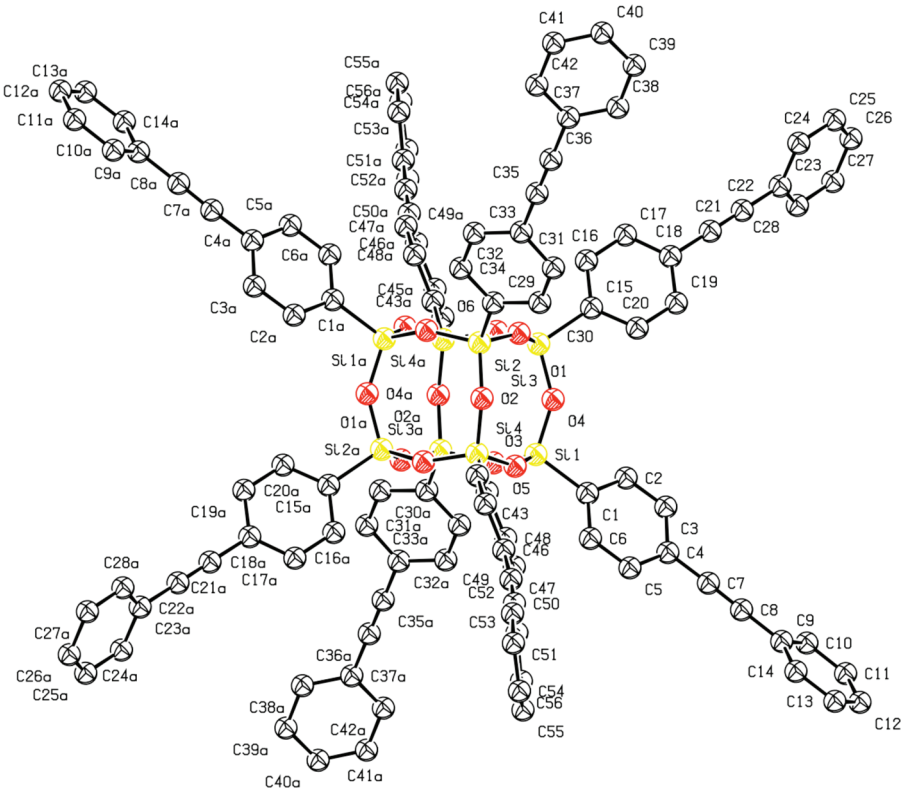


Figure 2. 50% thermal ellipsoid plots of $DPA_8OS \cdot 5m$-xylene. Hydrogen atoms and toluene solvates are omitted for clarity. Full XRD data can be found in the Supporting Information.

(Ph_6C_6) is a well-known quantitative reaction.[69] The high reaction temperature required leads to use of diphenyl ether as solvent (bp 260 °C).[32,33] Although tetraphenylcyclopentadienone is available commercially, to improve solubility in subsequent derivatives the (p-$Tolyl_5PhC_6$)$_8$OS (see Experimental Section) was synthesized via the condensation of the tolylethyne derivative with tetra(p-tolyl)cyclopentadienone. Tetra(p-tolyl)cyclopentadienone[70] was synthesized in two steps using modified literature methods.[71,72]

The DMAP-catalyzed condensation of p-tolylacetic acid by DCC, reported by Bhandari and Ray, was modified and used to synthesize ditolylacetone.[71] Modifying the published preparation for tetraphenylcyclopentadieneone,[72] the recrystallized di(p-tolyl)acetone was condensed with 4,4′-dimethylbenzil in refluxing ethanol with catalytic amounts of KOH (Scheme S.1). The product was recrystallized twice and washed repeatedly with methanol until all traces of base were eliminated. The product was characterized by ^{1}H NMR and found to be pure.

The condensation of the diarylethynyl-substituted OS with the respective tetraarylcyclopentadienone was conducted in refluxing phenyl ether, per Scheme 2. In each case, the reaction was found to be complete after 24 h. Condensation of **1a** with tetraphenylcyclopentadienone gives the unsubstituted

Table 2. Crystal Structure Refinement Data for $DPA_8OS \cdot 5$ *m*-xylene

	$DPA_8OS \cdot 5m$-xylene
space group	P-1, triclinic
unit cell dimensions	a = 14.4668(9) Å
	b = 15.5858(10) Å
	c = 15.9361(10) Å
	α = 70.874(1)°
	β = 88.818(1)°
	γ = 64.954(1)°
unit cell volume	3216.5(4) Å^3
Z	1
R-factor	5.5% (10.0%)[a]

[a] Before use of SQUEEZE to account for disordered solvent.

(Ph_6C_6)$_8$OS. Following precipitation of the reaction mixture into cold methanol, recrystallization was readily effected by slow cooling of hot, saturated toluene or mesitylene solutions.

Figure S.8 shows the ^{1}H spectrum of the (Ph_6C_6)$_8$OS. The aromatic resonances are found between 6 and 7 ppm, consistent with the single proton resonance of Ph_6C_6 at 6.8 ppm.[73] Figure S.9

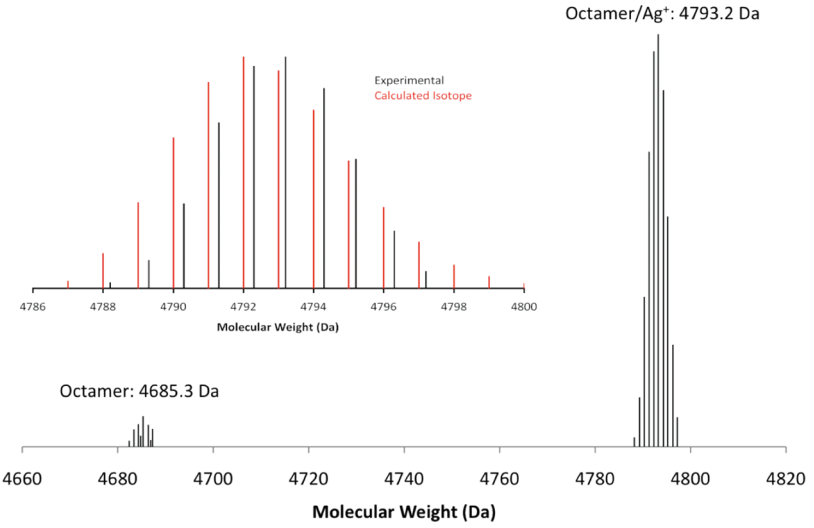


Figure 3. MALDI-TOF spectrum of $(Ph_6C_6)_8OS$ (Ag^+/dithranol).

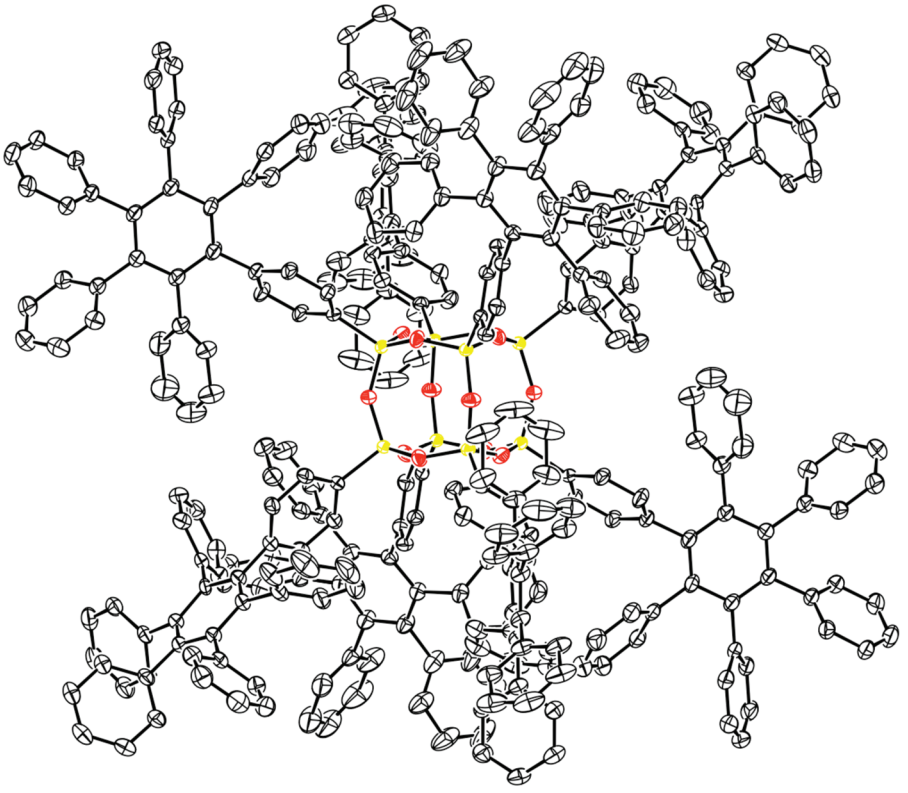


Figure 4. 50% thermal ellipsoid plots of $(Ph_6C_6)_8OS \cdot 18$toluene. Labels, hydrogen atoms, and toluene solvates are omitted for clarity. Full XRD data can be found in the Supporting Information.

shows the ^{13}C spectrum of $(Ph_6C_6)_8OS$, with 13 resolved peaks, which correspond well to the reported shifts for hexaphenylbenzene.[73] Figure 3 shows the MALDI-TOF spectrum of 56 Aryl, the symmetric octamer, and $(Ph_6C_6)_7PhOS$ to the left.

$(Ph_6C_6)_8OS$ crystallizes readily from hot toluene, providing crystals suitable for single crystal X-ray analysis (see Figure 4). The structure solution was refined to an *R*-factor of 5.7%. Large channels filled with 18 disordered toluene solvates comprise 55% of the crystal volume. These were modeled using the PLATON software package.[74] Additional crystallographic details are found in Table 3. The crystal structure shows open channels along the *a* and *b* crystallographic axes of 1 and 0.5 nm diameter, respectively, and these channels open into large voids between the molecules. The toluene quickly desorbs from the crystal, and powder diffraction indicates that this crystal structure collapses. The molecules are luminescent, and the photophysical behavior will be discussed in greater detail in the future.

Table 3. Crystal Structure Refinement Data for $(Ar_6C_6)_8OS$ Compounds

	$(Ph_6C_6)_8OS$	$(p\text{-Tolyl}_4Ph_2C_6)_8OS$
space group	*P*-1, triclinic	*P*4/*n*, tetragonal
unit cell dimensions	a = 21.6705(18) Å	a = 32.6146(19) Å
	b = 22.7273(19) Å	b = 32.6146(19) Å
	c = 27.648(2) Å	c = 41.178(5) Å
	α = 70.847(1)°	α = 90°
	β = 88.818(1)°	β = 90°
	γ = 64.954(1)°	γ = 90°
unit cell volume	11544.0(16) Å^3	43802(6) Å^3
Z	1	4
R-factor	5.7% (28.7%)[a]	12%

[a] Before use of SQUEEZE to account for disordered solvent.

$(p\text{-Tolyl}_5PhC_6)_8OS$ was synthesized by condensing **1b** with recrystallized tetra(*p*-tolyl)cyclopentadienone. Figure S.10 shows the ^1H spectrum of the $(p\text{-Tolyl}_5PhC_6)_8OS$. The aromatic resonances are again found between 6 and 7 ppm. However, there are two different benzylic proton resonances seen.

The integrations appear to correspond to the "inner" methyl groups, closer to the cage, and the "outer" methyl groups. Figure 5 provides a schematic of the chemical environments occupied by the different methyl groups. The aromatic resonance at 6.85 ppm would appear to correspond to the protons adjacent to the C−Si bond. The resonances at 6.55 and 6.45 ppm appear to correspond to the two inner aromatic rings. Figure 6 shows the MALDI-TOF spectrum of $(p\text{-Tolyl}_5PhC_6)_8OS$, indicating the symmetric octamer.

$(p\text{-Tolyl}_4Ph_2C_6)_8OS$ was synthesized by condensing **1a** with recrystallized tetra(*p*-tolyl)cyclopentadienone. Figure S.11 shows

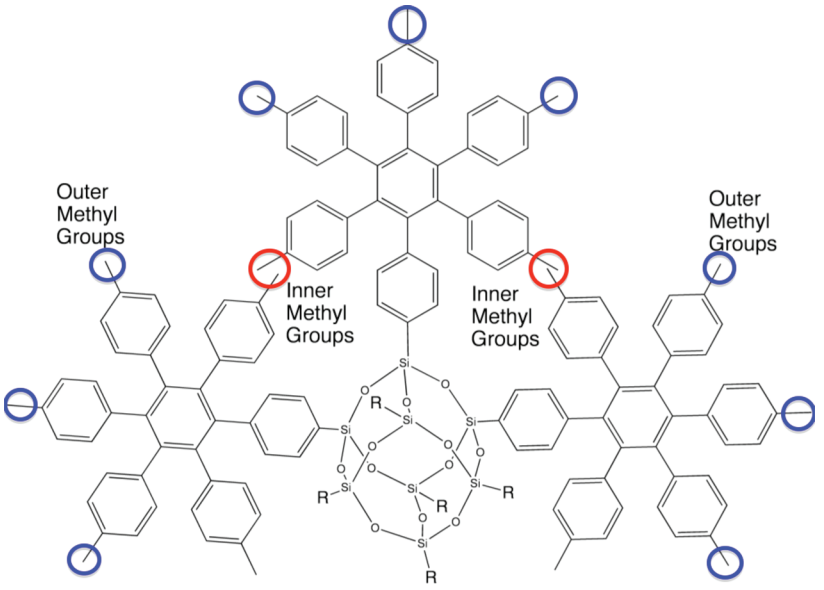


Figure 5. Depiction of methyl group environments in permethyl-56 Aryl.

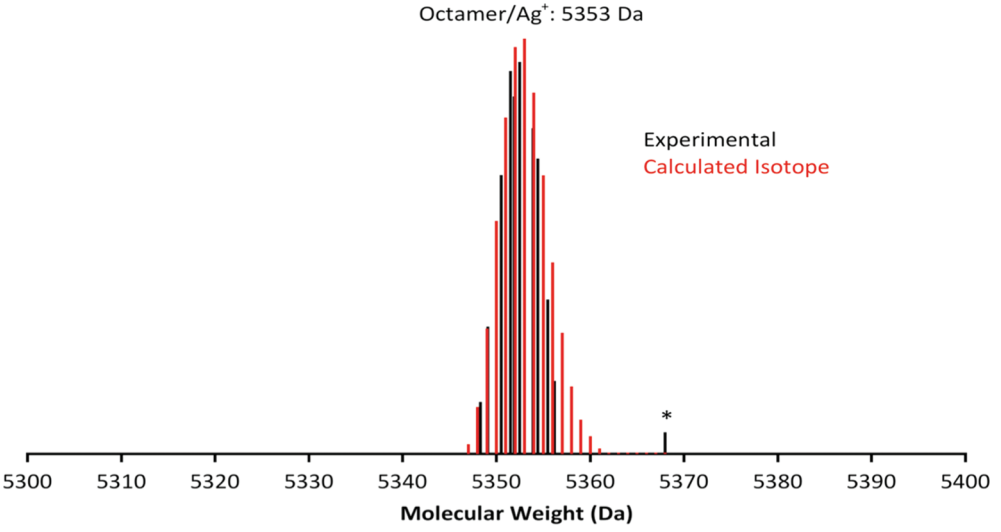


Figure 6. MALDI-TOF spectrum of $(p\text{-Tolyl}_5PhC_6)_8OS$ (Ag^+/dithranol).

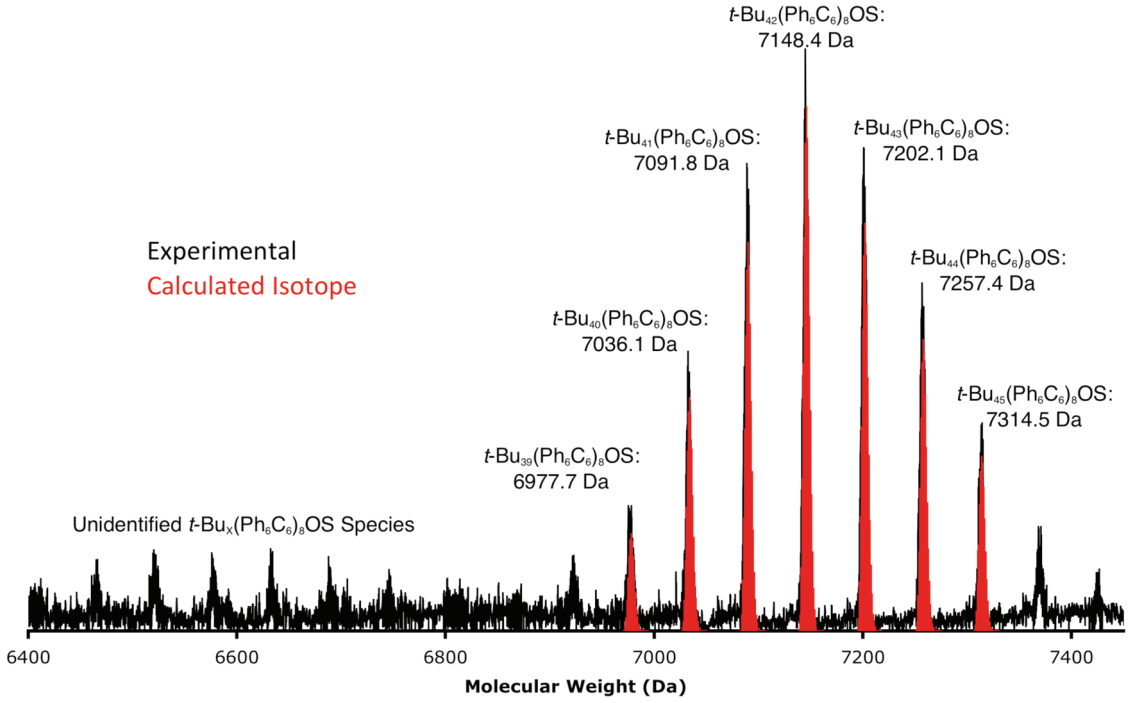


Figure 7. MALDI-TOF spectrum of the *tert*-butylated 56 Aryl (Ag^+/dithranol).

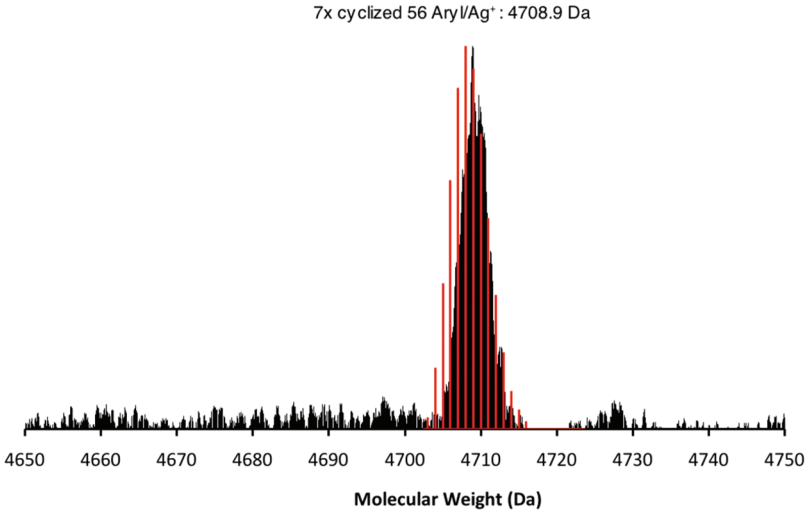


Figure 8. MALDI-TOF spectrum of the cyclized 56 Aryl.

the MALDI-TOF spectrum with the presence of an additional peak indicating partial functionalization of the parent alkyne. Figure S.12 shows the ^{1}H spectrum of the permethyl-56 Aryl compound. In this case, the aromatic resonances are again found between 6 and 7 ppm. As with the $(p\text{-Tolyl}_5\text{PhC}_6)_8\text{OS}$, there are two different benzylic proton resonances seen.

X-ray quality single crystals of $(p\text{-Tolyl}_4\text{Ph}_2\text{C}_6)_8\text{OS}$ were obtained from *m*-xylene/dodecane (see Figure S.13). The asymmetric unit consists of two independent molecules, but unfortunately the final *R*-factor was 12%. The solvent molecules are partially ordered, and two methyl groups are distributed over rotationally symmetric sites. Further data are included in the Supporting Information.

Since alkylated hexaarylbenzenes are often used as more soluble graphene precursors, a third derivative was synthesized. Rathore reported the *tert*-butylation of hexaphenylbenzene and its subsequent cyclization to form the hexa-*tert*-butylated hexa-*peri*-benzocoronene, in dichloromethane with a nitromethane solution of $FeCl_3$.[75] The direct application of this protocol led to overalkylated products as determined by ^{1}H NMR. Therefore, a milder catalyst, $SnCl_4$, was used.

$SnCl_4$ is known to be a selective *tert*-butylation catalyst, with a lower catalytic activity than $FeCl_3$ or $AlCl_3$.[76] The exhaustive alkylation of such a large macromolecule was difficult, and the proposed reaction required stoichiometric $SnCl_4$ and an excess of *tert*-butyl chloride and a 4 day reaction time in refluxing methylene chloride (Scheme S.2).

Aliquots were taken to monitor reaction progress, and after 4 days, the reaction was stopped when the integration of the

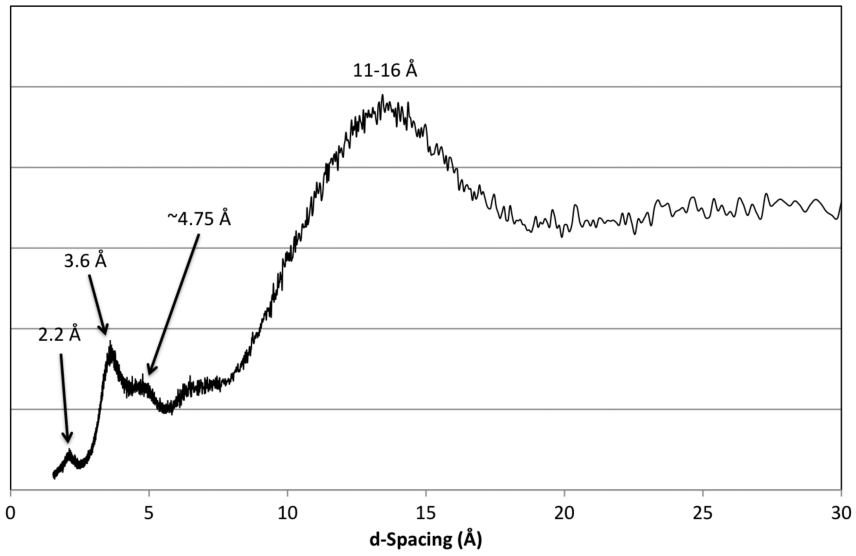


Figure 9. Powder XRD pattern of the cyclized $(p\text{-Tolyl}_5PhC_6)_8OS$.

alkyl and aromatic proton resonances corresponded to a total of ~40 *tert*-butyl groups per molecule (Figure S.12). The crude *tert*-butylated compound was recrystallized twice from hot acetone, giving a 30% yield as a white powder. Evaporation of the acetone allowed recovery of the less-crystalline component as a yellow, glassy solid. MALDI-TOF analysis of the crystalline fraction in Figure 7 shows an average of 42 *tert*-butyl groups per molecule.

Scholl Reaction Studies. Initial studies targeting cyclization of $(Ph_6C_6)_8OS$ (Scheme S.3) were disappointing, producing intractable red or red-black solids or no detectable reaction. Concurrent cyclization/*tert*-butylation studies were conducted to determine conditions for the efficient cyclization of these systems.[75] This ensured product solubility and allowed ^1H NMR analysis, a valuable tool for monitoring these reactions. Rathore et al. find that HBC derivatives exhibit aromatic resonances in the range of 9−10 ppm.[75] This large downfield shift from the hexaarylbenzene resonance at 6−7 ppm is due to increased ring currents in the delocalized π-system.[77−79]

^1H NMR analysis of the progress of the Scholl reaction revealed the need for several modifications to the standard conditions used by Rathore.[75] First, the reaction required heating to 40 °C to accelerate the reaction and increase the solubility of the silsesquioxanes after the addition of the nitromethane/$FeCl_3$ solution.

Second, an additional Lewis acid was necessary to scavenge the HCl produced during the reaction. This second improvement was suggested by the work of Kramer et al., who found that certain Scholl reactions were accelerated significantly by adding an HCl scavenger.[63] Thus, a 1.0 M solution of $SnCl_4$ in CH_2Cl_2 was used. These modifications allowed us to effect complete cyclization in 2 h. The reaction was then quenched by precipitation into cold methanol. The resulting precipitate was filtered and washed with an equal volume of 0.1 M methanolic HCl and two more volumes of methanol. The resulting solid was then dried under vacuum and analyzed.

These modifications were used to cyclize the *tert*-butylated 56 Aryl compound, providing a soluble product with the expected downfield shift in the aromatic proton resonance (Figure S.15). The integration of the *tert*-butyl protons is 77.5% of the sum of the alkyl and aromatic contributions, indicating roughly 95% conversion in comparison to theory, on average.

In contrast to the *tert*-butylated 56 Aryl compound, the cyclization of $(Ph_6C_6)_8OS$ led to a dark orange-red precipitate on quenching in methanol. The product was insoluble in all solvents, including hot *o*-dichlorobenzene and nitrobenzene. Using TCNQ as a matrix,[49] the (Figure 8) MALDI-TOF spectrum was obtained, indicating incomplete cyclization of the $(Ph_6C_6)_8OS$ precursor. The FTIR spectrum of this compound is shown in Figures S.16 and S.17. The presence of the ν Si−O−Si bands of the silsesquioxane core is seen from 1200 to 1000 cm^{-1}, and scaled to equivalent Si−O−Si band intensity, decreases in the ν ArC−H (3100−3000 cm^{-1}) bands suggest the loss of aromatic protons in the cyclization reaction.

In the case of the permethyl-56 Aryl compound, the cyclization gave a dark yellow precipitate on methanol quenching, which dried under vacuum to a brittle green-black solid. The product was again insoluble in all solvents, including hot *o*-dichlorobenzene and nitrobenzene. Grinding of the product by mortar and pestle provided a fine dark yellow powder for analysis by FTIR and powder X-ray diffraction.

The FTIR of this compound is shown in Figures S.18 and S.19. The presence of the ν Si−O−Si bands of the cage core is seen from 1200 to 1000 cm^{-1}, and scaled to equivalent heights Si−O−Si band intensity, several pronounced differences are seen between the two spectra. While the ν benzyl-H at 2915 cm^{-1} is unchanged in intensity, a dramatic decrease in the ν ArC−H bands (3100 to 3000 cm^{-1}), which is consistent with a loss of aromatic protons. Additionally, changes in the ν/δ C−C region 1600−1500 cm^{-1} are found as the absorbance at 1525 cm^{-1} decreases dramatically, and the intensity of the peak at 1600 cm^{-1} strongly increases.

Th powder XRD pattern of the cyclized $(p\text{-Tolyl}_5PhC_6)_8OS$ material is shown in Figure 9. Features are seen at *d*-spacings of 2.2, 3.6, 4.75, and 11−16 Å. The crystal structure of $(Ph_6C_6)_8OS$ indicates face and edge distances of 16.4 and 11.5 Å, between the Ph_6C_6 centroids. Since PAH molecules π stack nearly centroid-to-centroid, this is a reasonable approximation of the expected periodic spacing for cyclized $(p\text{-Tolyl}_5PhC_6)_8OS$ (Figure 10). These values correspond well to the broad *d*-spacing peak from 11 to 16 Å. The OS cage face and body diameters are 4.4 and 5.4 Å. In the hexa-*peri*-benzocoronene crystal structure, the $\pi\cdots\pi$ stacking distance between adjacent molecules is

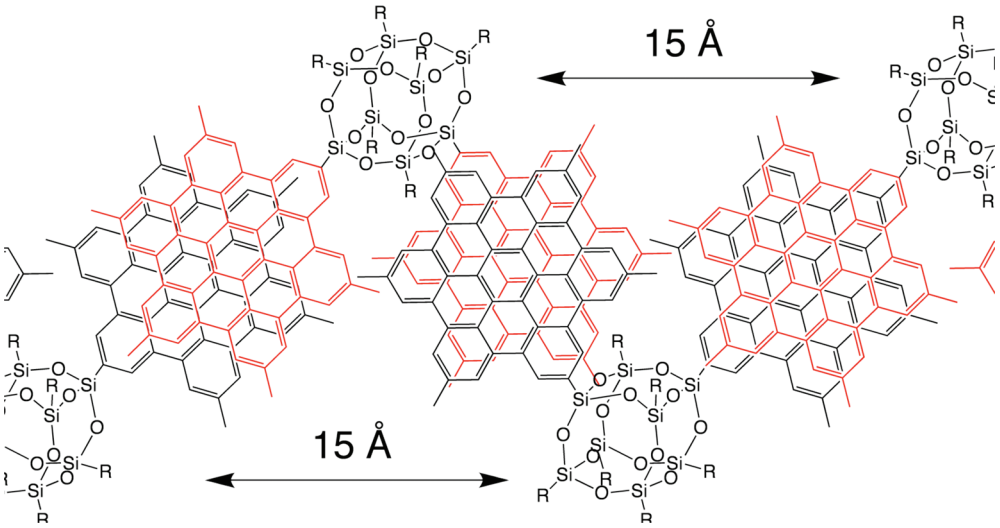


Figure 10. Diagram of possible *d*-spacings for the cyclized permethyl-56 Aryl.

3.4 Å,[80] which corresponds favorably to the feature at a *d*-spacing of 3.6 Å.

CONCLUSIONS

This report has detailed the synthesis and characterization of a unique set of highly conjugated silsesquioxanes derived from $(p\text{-IPh})_8$OS. The Sonogashira coupling of arylacetylenes with $(p\text{-IPh})_8$OS provides access to a number of ethynyl-functionalized Ph_8OS derivatives, including the octadiphenylacetyleneSQ and octa(*p*-methyldiphenylacetylene)SQ. OctadiphenylacetyleneSQ has been further characterized by single-crystal X-ray diffraction, with a refinement consistent with the proposed structure.

The high-temperature reaction of ethynyl-functionalized OPS with tetraarylcyclopentadienones provides the octa(hexaarylbenzene)SQs in essentially quantitative yield. Recrystallization of the octa(hexaphenylbenzene)SQ, or $(Ph_6C_6)_8$OS, gives single crystals suitable for X-ray diffraction and allows for a structural determination. More than half of the unit cell of $(Ph_6C_6)_8$OS consists of ~18 disordered toluene solvates, and open channels are found along the *ab*-plane.

Finally, dehydrogenative cyclization of the $(Ar_6C_6)_8$OS compounds leads to highly insoluble products. The more disordered *t*-$Bu_{40}(Ph_6C_6)_8$OS may be cyclized to provide a soluble product, which may be characterized by ^{1}H NMR. In each case, some loss of aromatic protons may be ascertained by FTIR or ^{1}H NMR, consistent with the proposed reaction.

These conjugated materials possess delocalized π-systems and may be suitable for use as active components in microelectronic systems. The octa-functionality could allow for intermolecular cooperative effects. The high thermal stability of the silsesquioxane cage should provide high stability at microelectronic operating temperatures.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental methods, characterizations, and fluorescent imaging procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

Dedicated to the memory of Professor Robert Bau, a mentor and friend.

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