NMR Data of ONPS and OAPS

As shown in Figure 1, new peaks appear in the $^1$H NMR after the reduction of ONPS, which can be assigned to NH$_2$ groups. Likewise, the aromatic peaks of ONPS disappear completely and new peaks appear at higher magnetic fields due to the electron donor properties of the amino groups (the integration ratio of peaks for the amino groups and the aromatic groups \( \approx 2:4 \)). The results support the quantitative reduction of the nitro groups to amino groups. The $^{13}$C-NMR results also support this process; peaks related to ONPS are replaced with peaks at higher field at the end of the reaction (Figure 2).

The ratio of isomers was calculated based on the assumption that the ratio of OAPS should be the same as that in ONPS. $^1$H- and $^{13}$C-NMR of ONPS were used to determine this ratio. Ten aromatic peaks were observed in the $^{13}$C-NMR spectra, with three insignificant peaks. The primary peaks in the $^{13}$C-NMR spectra correspond to ten different carbon environments for the meta and para isomers. The steric and electron-withdrawing effects of the silsesquioxane core (the same as –CF$_3$ group \(^4\)) are expected to severely inhibit the formation of the ortho isomer.

The $^1$H-NMR spectrum of ONPS shows multiple aromatic peaks. Among them, triplet peaks centered at 8.73 ppm can be assigned to protons between the nitro group and the siloxy group in the meta isomer. Assuming that the ortho component is negligible, the ratio of meta to para was calculated as essentially equal: 52% to 48%.
Figure 1. $^1$H-NMR spectra of (a) Octa(nitrophenyl)- and (b) Octa(aminophenyl)-silsesquioxane
Figure 2. $^{13}$C-NMR of (a) Octa(nitorophenyl)- and (b) Octa(aminophenyl)-sil sesquioxane

FTIR Data for ONPS and OAPS

The FT-IR spectra also support quantitative conversion (Figure 3). The ONPS spectrum shows two peaks at 1350 and 1530 cm$^{-1}$ assigned to symmetric and asymmetric vN=O. These peaks disappear completely after reaction and a new broad peak appears at 3375 cm$^{-1}$ that is assigned to vN-H appears.
Figure 3. FT-IR spectra of (a) ONPS and (b) OAPS

OAPS Reaction Products, Syntheses and Characterization Studies
Synthesis of octa(phthalimidephenyl)silsesquioxane (OPIPS): In a 25 ml schlenk, were placed OAPS (0.5 g, 0.433 mmol), phthalic anhydride (0.539 g, 3.64 mmol) and 5 ml of N-methylpyrrolidone. The mixture was stirred at room temperature for 5 min and then transferred to an aluminum container and heated in a vacuum oven under nitrogen up to 130 °C at a ramp rate of 5 °C/min and kept at temperature for 2h. Then, the sample was heated to 350 °C at a ramp rate of 5 °C/min and kept at temperature for 4h. After cooling to room temperature, the mixture was dissolved in 10 ml of dichloromethane and precipitated into 100 ml of hexane. Yield 0.764 g (0.348 mmol, 80.4%). ¹H-NMR (CDCl₃, ppm): 8.2-6.4 (b); ¹³C-NMR (CDCl₃, ppm): 166.7, 137.0, 133.8, 131.8, 128.7, 123.5; ²⁹Si-NMR (CH₂Cl₂, TMS, acetone-d₆, ppm): -80.8 (broad); Anal. Calc. for Si₈O₂₇C₁₁₂N₈H₆₄: C 61.3%, H 2.94%, N 5.11%; Found, C 60.0%, H 2.90%, N 5.17%; Ceramic yield (1000 °C/air) 22.1% (calc 21.9%); GPC Mn 1673, Mw 1931, Disp 1.16.

¹H-NMR confirms and ¹³C-NMR shows new aromatic carbons and one carbonyl carbon. The FT-IR clearly shows symmetric and asymmetric peaks for νC=O at 1786 and 1722 cm⁻¹, respectively. A peak for νC-N is observed at 1370 cm⁻¹. Since no original peaks from OAPS are seen in the ¹³C-NMR, all of the amino phenyl groups appear to react.

The TGA ceramic yield (air) was 22.1% vs 21.9% by theory, suggesting quantitative conversion. GPC molecular weight of OPIPS shows a smaller molecular weight than the calculated value due to the different hydrodynamic volumes. However, both Mn and Mw increase compared to OAPS while the polydispersity remains narrow, indicating retention of the cube structure. The fact that we have meta and para substituents likely accounts for the PD seen.

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All of these results support the effective conversion of the amino phenyl groups on OAPS to phthalimide groups.

Synthesis of octa(maleimidephenyl)silsesquioxane (OMIPS): In a 25 ml schlenk flask equipped with a condenser, were placed maleic anhydride (0.340 g, 3.46 mmol) and OAPS (0.5g, 0.433 mmol) and 7.5 ml of DMAc (N₂). The mixture was stirred at room temperature for 1 h under N₂ to dissolve the compounds. Acetic anhydride (0.820 ml, 8.68 mmol) and triethylamine (0.071 ml, 0.868 mmol) were added. The mixture was then heated at 60 °C for 3h under N₂. After cooling to room temperature, ethyl acetate (30 ml) was added and the resulting solution was washed with water (20 ml × 2). The separated organic layer was dried over sodium sulfate (~1 g) and precipitated into hexane (200 ml). The powder was collected by filtration and dried under vacuum at room temperature. Yield 0.616 g (0.343 mmol, 79.1 %). ³¹H-NMR (acetone-d₆, ppm): 8.2-7.2 (b, 4H), 6.98 (s, 1.8H), ¹³C-NMR (acetone-d₆, ppm): 170.34, 137.10, 135.19, 134.03, 132.65, 129.73; ²⁹Si-NMR (CH₂Cl₂, TMS, acetone-d₆, ppm): -80.26 (broad); Anal. Calc. for Si₈O₃₂C₇₀N₈H₄₈: C 53.6 %, H 2.70 %, N 6.25 %; Found, C 52.2 %, H 3.15 %, N 6.17 %; ceramic yield (1000 °C/air 26.4 % (calc 26.8 %); GPC Mn 1648, Mw 2042, Disp 1.24.

OAPS reacts with maleic anhydride at room temperature in N,N-dimethylacetamide (DMAc) to form the amic acid. Dehydration with acetic anhydride is used to form the imide ring. ¹³H-NMR spectrum demonstrated disappearance of the NH₂ peak and appearance of vinyl protons at 7.0 ppm. The carbonyl group was also observed in ¹³C-NMR at 170.3 ppm. IR showed the imide νC=O at 1787, 1722 and a νC-N band at 1377 cm⁻¹. The TGA ceramic yield and the elemental analysis data agree very well with the calculated value (26.4 % vs 26.8 % theory). These results suggest the quantitative conversion of OAPS to the maleimide analogous. The GPC trace indicates a small amount of a second product, perhaps a dimer formed by maleamide bridging of two cubes, which causes a higher polydispersity in the GPC data.

Synthesis of N-fluorene-OAPS (OFPS): OAPS (0.5 g, 0.434 mmol, -NH₂ 3.47 mmol), 2-bromo-9,9'-dimmethylfluorene (synthesized as described below) (1.042 g, 3.81 mmol), tris(dibenzylidene-acetone)dipalladium (0) (46.7 mg, 0.208 mmol), dicyclohexylphosphininophenyl (80.2 mg, 0.229 mmol) were placed in a 50 ml flask equipped with a condenser and purged with nitrogen. The mixture was dissolved in 8 ml of dry ethylene glycol dimethyl ether. The mixture was heated at 100 °C for 5.5 h. After cooling to room temperature, 8 ml of ethyl acetate was added and the solution was washed with 20 ml of water twice and then 20 ml of brine. The organic layer was dried over ~1 g of Na₂SO₄ and precipitated into 100 ml of hexane. The recovered powder was dissolved in 1 ml of THF and put through a silica column (5 × 1 cm) to remove catalyst. The solution was condensed to 10 ml and precipitated into 100 ml of hexane. White powder was collected by filtration and vacuum dried. Yield 0.378 g, (87.1 %). (Yield was calculated assuming conversion degree of 0.66 fluorenes per nitrogen and molecular weight of 2160.7). ¹³H-NMR (acetone-d₆, ppm): 8.0-6.8 (m, 12.2 H), 6.6 (b, 0.86 H), 4.80 (b, 0.37 H), 3.7 (b, 0.16 H), 1.30 (b, 6.0 H); ¹³C-NMR (acetone-d₆, ppm) 155.9, 153.8, 143.8, 140.2, 136.5, 132.7, 129.8, 127.7, 126.6, 124.6, 123.2, 121.6, 119.7, 117.1, 116.1,
112.8, 47.2, 27.5; $^{29}$Si-NMR (TMS, acetone-<i>d</i>$_6$, ppm): -77.3, -78.8 (broad); Anal. Calc. for Si$_8$O$_{12}$C$_{272}$N$_{10}$H$_{136}$: C 70.7%, H 4.82%, N 5.19%; Found, C 70.9%, H 4.80%, N 4.07%; ceramic yield (1000 °C/air) 21.2% (calc 22.2%); GPC Mn 2614, Mw 2981, Disp 1.14.

**Synthesis of 2-Bromo-9,9'-dimethylfluorene:** To DMSO (40 ml) solution of 2-bromofluorene (purchased from Aldrich Chemical Company, Inc.) (10 g, 40.8 mmol) were added aqueous NaOH (20 g of NaOH and 20 ml of H$_2$O), benzyltrimethylammonium hydroxide (40 wt % methanol solution, 1.02 ml, 2.24 mmol) and methyl iodide (14.0 ml, 224 mmol) under N$_2$. The mixture started refluxing after addition of methyl iodide. After 10 min, methyl iodide (14.0 ml, 224 mmol) was added again and the mixture was left to reflux. After 2h, the mixture stopped refluxing and was heated at 80 °C for 1h with addition of more methyl iodide (14.0 ml, 224 mmol). After cooling to room temperature, 100 ml of water and 150 ml of ether were added and the mixture was stirred vigorously for 30 min. After removal of the aqueous layer, the organic layer was washed with saturated NaCl until neutral and dried over MgSO$_4$. The solvent was evaporated under reduced pressure. The product was obtained as slightly yellow crystalline from recrystallization in ethanol with a few drops of THF. Yield 8.5 g (31.1 mmol, 76.2%). $^1$H-NMR (CDCl$_3$, ppm): 7.69 (m, 1.0 H), 7.57 (m, 1.9 H), 7.46 (dd, 1.0 H), 7.42 (m, 1.0 H), 7.34 (m, 2.0 H), 1.47 (s, 7.3 H); $^{13}$C-NMR (CDCl$_3$, ppm): 155.6, 153.2, 138.2, 138.1, 130.1, 127.6, 127.1, 126.1, 122.6, 121.3, 121.0, 120.0, 47.1, 27.0; MS m/z 275 (13), 274 (M$^+$, 68), 273 (14), 272 (M$^+$, 70), 260 (13), 259 (72), 258 (14), 257 (71), 178 (100); Anal. Calcd for C$_{15}$H$_{13}$Br: C, 65.95%; H, 4.80. Found: C, 66.22; H, 4.79

The reaction mixture was heated at 100 °C for 5.5 h and purified by precipitation in hexane and then by silica column chromatography. $^1$H-NMR showed the methyl groups from the fluorene moiety at 1.3 ppm, from which the conversion degree was calculated as 0.66 per nitrogen. GPC result shows the increase of the molecular weight and the retention of the cubic structure as observed as a unimodal sharp peak. Instead of a broad NH$_2$ peak at 3375 cm$^{-1}$, a sharper N-H peak appeared at 3416 cm$^{-1}$. Besides an aromatic vC-H peak at 3056 cm$^{-1}$, several aliphatic vC-H peaks appeared at 2965, 2730 and 2876 cm$^{-1}$. The peak positions for aromatic C-C stretching also changed completely (not shown).

**Schiff base (OSPS):** 2-pyridinecarboxaldehyde (0.442 ml, 4.68 mmol) was added to a THF (4.5 ml) solution of OAPS (0.45 g, 0.39 mmol, -NH$_2$ 3.12 mmol,) at 0 °C under N$_2$. After adding 177.2 mg (1.25 mmol) of sodium sulfate, the mixture was stirred at RT for 22 h. The salt was filtered off and the solution precipitated into 50 ml of hexane. White powder was collected by filtration. Yield 0.573 g (0.307 mmol, 79%). $^1$H-NMR (CDCl$_3$, ppm): 8.6 (b, 1.0 H), 8.5-6.2 (broad multiplet, 14.5 H); $^{13}$C-NMR (CDCl$_3$, ppm) 160.4, 154.6, 149.7, 136.7, 132.7, 129.1, 127.0, 125.1, 123.0, 122.2. $^{29}$Si-NMR (CH$_2$Cl$_2$, TMS, acetone-<i>d</i>$_6$, ppm): -78.7 (broad); Anal. Calc. for Si$_8$O$_{12}$C$_{98}$N$_{12}$H$_{172}$: C 61.8%, H 3.89%, N 12.0%; Found, C 58.3%, H 3.94%, N 11.3%; ceramic yield (1000 °C/air) 24.8% (calc 25.7%); GPC Mn 1056, Mw 1098, Disp 1.04.

$^1$H-NMR shows quantitative conversion as observed by the disappearance of the amine peak and appearance of the proton adjacent to the imine group at 8.6 ppm. The $^{13}$C-NMR also
supports complete reaction as the peak positions are altered completely after the reaction. FT-IR showed disappearance of NH$_2$ (3375 cm$^{-1}$) and appearance of a new peak at 1633 cm$^{-1}$ for vC=N peak among with other new aromatic vC=C peaks.

Table 2. Degree of Derivitization

<table>
<thead>
<tr>
<th>Cubic silsesquioxanes</th>
<th>The degree of derivatization</th>
<th>Yield (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ONPS</td>
<td>Quantitative a)</td>
<td>90.1 %</td>
</tr>
<tr>
<td>OAPS</td>
<td>Quantitative a)</td>
<td>82.0 %</td>
</tr>
<tr>
<td>OPIPS</td>
<td>Quantitative a)</td>
<td>80.4 %</td>
</tr>
<tr>
<td>OMIPS</td>
<td>Quantitative a)</td>
<td>79.1 %</td>
</tr>
<tr>
<td>OFPS</td>
<td>66.0 % b)</td>
<td>87.1 %</td>
</tr>
<tr>
<td>OSPS</td>
<td>Quantitative a)</td>
<td>79.0 %</td>
</tr>
</tbody>
</table>

a) Based on $^1$H/$^{13}$C-NMR, TGA and elemental analysis. b) Calculated from $^1$H-NMR.