SUPPORTING INFORMATION FOR

Soluble Polycyclosilane-polysiloxane Hybrid Material and Silicon Thin Film Having Optical Properties at 193 nm and Etch Selectivity

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1.1. Materials and instruments.

In all reactions in which air-sensitive chemicals were used, the reagents and solvents were dried prior to use. THF, diethyl ether, benzene, triethylamine and n-hexane were distilled from Na/Ph3CO, and EtOH was distilled from calcium hydride. Other starting materials were purchased as reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. All manipulations were performed using standard Schlenk techniques under a nitrogen or argon atmosphere and using a Glove box (MBraun). 1H, 13C and 29Si NMR spectra were recorded using a Bruker Avance II+ BBO 400 MHz SI spectrometer. The chemical shifts were referenced to internal C6D6, CDCl3 or external tetramethylsilane. All solid-state NMR experiments were conducted on NMR instruments (Varian unity NOVA, USA) using 5 mm and 2.5 mm double resonance MAS probeheads for 29Si and 1H at 14.1 T (1H resonance frequency 600 MHz, wide bore) at room temperature. Mass spectra were recorded on a low-resolution (Agilent Technologies GC/MS: 6890N, 5973N mass selective detector) EI mass spectrometer and a high-resolution (JEOL JMS-600W Agilent 6890 Series) instrument. UV-Vis Spectra were obtained using a Lambda 25 UV-Vis spectrometer (Perkin-Elmer). Gel permeation chromatography (GPC) was performed using Younglin YL 9100 high-performance liquid chromatography (HPLC) with Shodex KF-800 series columns, and a Younglin YL 9170 refractive index (RI) detector with HPLC grade THF as solvent (Burdick & Jacobsen). Polystyrene was used as GPC standard, which was purchased from Shodex. IR spectra were recorded on a Perkin Elmer Spectrum one B Fourier transform infrared (FT-IR) spectrophotometer. Spin coating was performed using a Mikasa MS-A150 spin coater. The n (refractive index) and k (extinction coefficient) values were measured by a Ellipsometer VB-400 made by J. A. Woollam Co., Inc. Etch rates against both N2/O2 and CF4 plasma were measured using a TCP9400DFM Poly Chamber (Lam Research Corporation). The conditions for N2/O2 plasma were 50 mT / 27 MHz 300 W / 2 MHz 0 W / 40 O2 / 20 N2 / 500 Ar/ 10 sec and the conditions for CF4 plasma were 200 mT / 27 MHz 600 W / 2 MHz 850 W / 800 Ar / 50 CF4 / 80 CHF3 / 10 CH2F2 / 20 O2 / 10 sec. The film mass density was calculated from X-ray reflectivity (XRR) by using a XPert PRO MPD (Panalytical, Nederland). X-ray photoelectron spectroscopy (XPS) measurements were taken by a K-alpha (Thermo U. K.) with a monochromated Al Kα source (1486.6 eV) under ultrahigh vacuum conditions.
1.2. Synthesis of 3.
EtOH (8.6 ml, 0.15 mol) and Et$_3$N (25.5 ml, 0.18 mol) dissolved in diethylether (100 ml) were slowly added to the mixture of 2 (5.7 g, 12.2 mmol) dissolved in diethylether (300 ml) for 1 h at -78 °C. After the mixture had been stirred for 6 h at -78 °C and slowly warmed up to room temperature, the solution was stirred for 12 h at that temperature. The Et$_3$N$^+$Cl$^-$ salt was removed by filtration and washing with n-hexane at argon atmosphere in a Glove box, and volatiles were distilled under vacuum. Two geometric isomers of 3 were obtained as white solid in 25.8% yield and pale green oil in 74.2% yield (5.6 g, 86%). Me$_6$Si$_6$(OEt)$_6$ (3):

$^1$H NMR (C$_6$D$_6$, 400 MHz): \(\delta\) 3.57-3.97 (m, 12H, SiOCH$_2$CH$_3$), 1.10-1.29 (m, 18H, SiOCH$_2$CH$_3$), 0.41-0.88 (m, 18H, SiCH$_3$).

$^{13}$C NMR (C$_6$D$_6$, 100 MHz): \(\delta\) -2.05-1.69 (m, Si-CH$_3$), 18.91-26.15 (m, Si-OCH$_2$CH$_3$), 58.34-68.15 (m, Si-OCH$_2$CH$_3$).

$^{29}$Si NMR (C$_6$D$_6$, 79 MHz): \(\delta\) 2.89-9.79 (m). HRMS: C$_{18}$H$_{48}$O$_6$Si$_6$ 528.2067 (M$^+$/calcld), 528.2073 (found), 528.2077 (found). MS: \(m/z\) (relative intensity): 528 (M$^+$, 4.1), 499 (25.0), 455 (10.4), 323 (100), 263 (39.6), 133 (35.4), 89 (20.8). The single crystals of all-cis 3 were obtained by recrystallization from n-hexane at -20 °C. All-cis 3: $^1$H NMR (C$_6$D$_6$, 400 MHz): \(\delta\) 3.94 (q, 12H, SiOCH$_2$CH$_3$), 1.27 (t, 18H, SiOCH$_2$CH$_3$), 0.50 (s, 18H, SiCH$_3$).

$^{13}$C NMR (C$_6$D$_6$, 100 MHz): \(\delta\) -1.56 (Si-CH$_3$), 19.30 (Si-OCH$_2$CH$_3$), 62.04 (Si-OCH$_2$CH$_3$). $^{29}$Si NMR (C$_6$D$_6$, 79 MHz): \(\delta\) 4.22 (s).

1.3. Synthesis of hybrid of polycyclosilane-polysiloxane compounds and preparation of thin films.
MTMS (methyltrimethoxysilane) was dissolved in PGMEA (propylene glycol monomethyl ether acetate) with 10 wt% concentration. An acid catalyst (100 ppm HNO$_3$ per H$_2$O mol) aqueous solution (3 eq H$_2$O per mol of MTMS) was added. The hydrolysis reaction was carried out for 6 h at room temperature and then H$_2$O and MeOH were removed by evaporation. Geometric isomers of 3 were dissolved in PGMEA with 10 wt% concentration, which was then added to hydrolyzed MTMS. The hydrolysis and condensation reaction was carried under controlled temperature conditions (r.t.-120 °C) for 1-2 weeks to control the molecular weight of hybrid of polysiloxane-polysilicon compounds. The reaction was checked continuously by GPC. By products (EtOH and MeOH) were removed by evaporation and solution diluted in PGMEA to 4 wt% concentration. Thin films of 4a, 4b and 4c were prepared by spin coating on silicon wafers (4 inch or 8 inch) and baking at 200 °C for 1 minute using 4a, 4b and 4c solutions, respectively.
2. X-ray Crystallography Detail

Figure S1. ORTEP Diagram of all-trans 2.

Table S1. Bond lengths [Å] for all-trans 2.

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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1 Si2</td>
<td>2.3359(16)</td>
<td>Si2 C2'</td>
</tr>
<tr>
<td>Si1 Si3</td>
<td>2.3356(16)</td>
<td>Si2 C2</td>
</tr>
<tr>
<td>Si1 Cl1</td>
<td>2.001(4)</td>
<td>Si2 Cl2'</td>
</tr>
<tr>
<td>Si1 Cl1'</td>
<td>1.869(15)</td>
<td>Si3 Si1</td>
</tr>
<tr>
<td>Si1 Cl1'</td>
<td>1.887(16)</td>
<td>Si3 Cl3</td>
</tr>
<tr>
<td>Si1 Cl1'</td>
<td>2.064(3)</td>
<td>Si3 C3'</td>
</tr>
<tr>
<td>Si2 Si3</td>
<td>2.3390(16)</td>
<td>Si3 C3</td>
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<tr>
<td>Si2 Cl2</td>
<td>2.078(3)</td>
<td>Si3 Cl3'</td>
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Table S2. Bond angles [°] for all-trans 2.

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<tr>
<th></th>
<th>Si2 Si1 Si3</th>
<th>Cl2 Si2 Si1</th>
<th>Cl2 Si2 Si3</th>
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<td>Si1 Si2</td>
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<td>105.38(15)</td>
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<td>108.41(18)</td>
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<td>Cl1 Si1 Si3</td>
<td>107.72(18)</td>
<td></td>
<td>110.4(8)</td>
</tr>
<tr>
<td>C1” Si1 Si2</td>
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<td></td>
<td>109.4(9)</td>
</tr>
<tr>
<td>C1” Si1 Si3</td>
<td>110.4(9)</td>
<td></td>
<td>109.4(9)</td>
</tr>
<tr>
<td>C1” Si1 Cl1’</td>
<td>104.6(8)</td>
<td></td>
<td>105.7(9)</td>
</tr>
<tr>
<td>C1 Si1 Si2</td>
<td>110.4(9)</td>
<td></td>
<td>117.6(8)</td>
</tr>
<tr>
<td>C1 Si1 Si3</td>
<td>111.0(9)</td>
<td></td>
<td>108.2(12)</td>
</tr>
<tr>
<td>C1 Si1 Cl1</td>
<td>107.8(7)</td>
<td></td>
<td>110.85(18)</td>
</tr>
<tr>
<td>Cl1’ Si1 Si2</td>
<td>106.76(16)</td>
<td></td>
<td>106.98(14)</td>
</tr>
<tr>
<td>Cl1’ Si1 Si3</td>
<td>108.19(17)</td>
<td></td>
<td>111.92(6)</td>
</tr>
<tr>
<td>Si1 Si2 Si3</td>
<td>110.81(6)</td>
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<td></td>
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**Table S3.** Crystal data and structure refinement for compound all-trans 2.

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>CCDC no.</td>
<td>984675</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₆H₁₈Cl₆Si₆</td>
</tr>
<tr>
<td>Formula weight</td>
<td>471.44</td>
</tr>
<tr>
<td>Temperature</td>
<td>100.0 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 17.7183(15) Å alpha = 90.00 °.</td>
</tr>
<tr>
<td></td>
<td>b = 9.8193(8) Å beta = 109.717(4) °.</td>
</tr>
<tr>
<td></td>
<td>c = 13.5232(12) Å gamma = 90.00 °.</td>
</tr>
<tr>
<td>Volume</td>
<td>2214.8(3) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.414 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>4.231 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>960.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.1 × 0.09 × 0.07 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.814 to 52.724°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-22 ≤ h ≤ 20, 0 ≤ k ≤ 12, 0 ≤ l ≤ 16</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>2316 / 2316[R(int) = 0.0439]</td>
</tr>
<tr>
<td>Completeness to theta = 26.362</td>
<td>102.1 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.746 and 0.641</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data/restraints/parameters</td>
<td>2316/103/108</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.143</td>
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<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0506, wR₂ = 0.1353</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0555, wR₂ = 0.1391</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.82 and -0.53 e.Å⁻³</td>
</tr>
</tbody>
</table>
Figure S2. ORTEP Diagram of all-cis 3.

Table S4. Bond lengths [Å] for all-cis 3.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Si1 Si2</td>
<td>2.368(5)</td>
<td>Si2 C2</td>
<td>1.879(13)</td>
<td></td>
</tr>
<tr>
<td>Si1 Si2</td>
<td>2.360(5)</td>
<td>O1 C3</td>
<td>1.366(17)</td>
<td></td>
</tr>
<tr>
<td>Si1 O1</td>
<td>1.619(13)</td>
<td>O2 C5</td>
<td>1.402(17)</td>
<td></td>
</tr>
<tr>
<td>Si1 C1</td>
<td>1.898(13)</td>
<td>C3 C4</td>
<td>1.463(18)</td>
<td></td>
</tr>
<tr>
<td>Si2 Si12</td>
<td>2.368(5)</td>
<td>C5 C6</td>
<td>1.38(3)</td>
<td></td>
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<tr>
<td>Si2 O2</td>
<td>1.644(14)</td>
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Table S5. Bond angles [°] for all-cis 3.

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<th>Bond Angles</th>
<th>Value</th>
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<td>Si2 Si1 Si2</td>
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<td>O2 Si2 Si1</td>
<td>109.6(5)</td>
</tr>
<tr>
<td>O1 Si1 Si2</td>
<td>105.4(5)</td>
<td>O2 Si2 C2</td>
<td>101.5(6)</td>
</tr>
<tr>
<td>O1 Si1 Si2</td>
<td>113.9(5)</td>
<td>C2 Si2 Si1</td>
<td>108.0(4)</td>
</tr>
<tr>
<td>O1 Si1 C1</td>
<td>109.0(6)</td>
<td>C2 Si2 Si1</td>
<td>110.2(4)</td>
</tr>
<tr>
<td>C1 Si1 Si2</td>
<td>110.6(4)</td>
<td>C3 O1 Si1</td>
<td>133.8(14)</td>
</tr>
<tr>
<td>C1 Si1 Si2</td>
<td>108.3(5)</td>
<td>C5 O2 Si2</td>
<td>137.3(15)</td>
</tr>
<tr>
<td>Si1 Si2 Si1</td>
<td>112.9(2)</td>
<td>O1 C3 C4</td>
<td>113.2(18)</td>
</tr>
<tr>
<td>O2 Si2 Si1</td>
<td>113.9(5)</td>
<td>O2 C5 C6</td>
<td>118(2)</td>
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Table S6. Crystal data and structure refinement for compound all-cis 3.

<table>
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<th>Property</th>
<th>Value</th>
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<tr>
<td>CCDC no.</td>
<td>984676</td>
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<tr>
<td>Empirical formula</td>
<td>C_{18}H_{48}O_{6}Si_{6}</td>
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<tr>
<td>Formula weight</td>
<td>529.10</td>
</tr>
<tr>
<td>Temperature</td>
<td>230.2 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, I-43d</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 23.3514(5) Å alpha = 90.00 °.</td>
</tr>
<tr>
<td></td>
<td>b = 23.3514(5) Å beta = 90.00 °.</td>
</tr>
<tr>
<td></td>
<td>c = 23.3514(5) Å gamma = 90.00 °.</td>
</tr>
<tr>
<td>Volume</td>
<td>12733.2(5) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>16, 1.104 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.288 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>4608</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.5 × 0.3 × 0.2 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.14 to 24.06°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-21 ≤ h ≤ 21, -21 ≤ k ≤ 21, -20 ≤ l ≤ 21</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>45859 / 901 [R(int) = 0.0719]</td>
</tr>
<tr>
<td>Completeness to theta = 24.06</td>
<td>98.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.941 and 0.930</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.060</td>
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<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R₁ = 0.0834, wR₂ = 0.2180</td>
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<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0902, wR₂ = 0.2289</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.483 and -0.256 e.Å⁻³</td>
</tr>
</tbody>
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3. NMR spectra

Figure S6. $^1$H NMR spectrum of 3.

Figure S7. $^{13}$C NMR spectrum of 3.
Figure S8. $^{29}$Si NMR spectrum of 3.

Figure S9. $^1$H NMR spectrum of all-cis 3.
Figure S10. $^{13}$C NMR spectrum of all-cis 3.

Figure S11. $^{29}$Si NMR spectrum of all-cis 3.
Figure S12. $^1$H CP/MAS NMR spectrum of film 4a.

Figure S13. $^1$H CP/MAS NMR spectrum of film 4b.
Figure S14. $^1$H CP/MAS NMR spectrum of film 4c.

Figure S15. $^{29}$Si CP/MAS NMR spectrum of film 4a.
Figure S16. $^{29}$Si CP/MAS NMR spectrum of film 4b.

Figure S17. $^{29}$Si CP/MAS NMR spectrum of film 4c.
Figure S18. Extinction coefficient (k) spectrum of film 4a.

Figure S19. Extinction coefficient (k) spectrum of film 4b.
Figure S20. Extinction coefficient (k) spectrum of film 4c.