

## Supplementary Materials

### **Novel Double Cored Oligosilane Dendrimers – Conformational Dependence of the UV Absorption Spectra**

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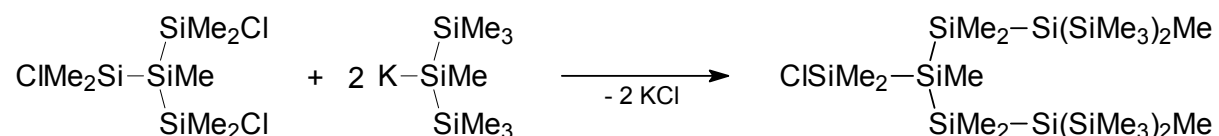
#### **Experimental**

The manipulation of air-sensitive compounds involved standard Schlenk line and dry box techniques. All solvents were freshly distilled under argon from alkali metals prior to use. Benzene-D<sub>6</sub> was dried over activated molecular sieves and stored in the glove box. MeSi(SiMe<sub>2</sub>Cl)<sub>3</sub> [1] and (ClMe<sub>2</sub>Si)<sub>2</sub>SiMe-SiMe(SiMe<sub>2</sub>Cl)<sub>2</sub> [2] were synthesized according to the literature procedures. <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were obtained from Bruker AC 250 and ARX 300 spectrometers using benzene-D<sub>6</sub> as solvent. MS: Intectra AMD 402. - UV/Vis in solution: Perkin Elmer Lambda 2, quartz cells of 1.0 cm path length and spectral grade n-heptane. Thin films are made on quartz plates from 10<sup>-2</sup> M hexane solutions and the spectra were recorded on a Perkin Elmer Lambda 900. The diffuse reflectance UV measurements were carried out with a Perkin Elmer Lambda 20.

#### 4-Chlorodimethylsilyl-1,1,1,2,3,3,4,5,5,6,7,7,7-tridecamethyl-2,6-bis(trimethylsilyl)heptasilane:

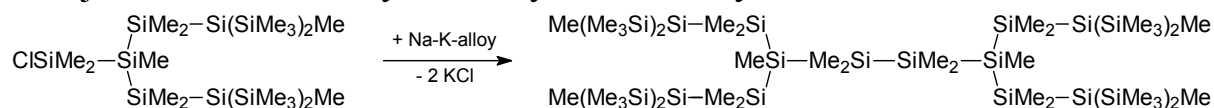
In a Schlenk flask with magnetic stirrer were placed rapidly MeSi(SiMe<sub>3</sub>)<sub>3</sub> (4.59 g, 17.5 mmol) and Bu<sup>t</sup>OK (1.96 g, 17.5 mmol). The flask was evaporated and refilled with argon three times, THF (40 mL) was added and the yellow solution of K-Si(SiMe<sub>3</sub>)<sub>2</sub>Me immediately formed was stirred overnight. After removal of the solvent and other volatiles under vacuum, the remaining solid was dissolved in pentane and transferred into a dropping funnel. This

solution was slowly dropped to a vigorous stirred and to  $-78^{\circ}\text{C}$  cooled pentane solution of  $(\text{ClMe}_2\text{Si})_3\text{SiMe}$  (2.84 g, 8.77 mmol). Stirring was continued for 30 min at  $-78^{\circ}\text{C}$  and the mixture was allowed to warm up to room temperature within 2 hours. After filtration and removal of the solvent, the residue was distilled under vacuum ( $180\text{-}190^{\circ}\text{C}$ , 0.01 mbar) to give 4.64 g (84%) of the title compound as highly viscous oil. -  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 250 MHz):  $\delta$  0.60 (s,  $\text{SiMe}_2\text{Cl}$ , 6 H), 0.52, 0.50, 0.33 (3s,  $\text{SiMe}_2$ ,  $3 \times 6$  H), 0.51 (s,  $\text{SiMe}$ , 3 H), 0.25, 0.24 (2s,  $\text{SiMe}_3$ ,  $2 \times 18$  H). -  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 62.9 MHz):  $\delta$  6.1 ( $\text{SiMe}_2\text{Cl}$ ),  $2 \times 1.1$  ( $\text{SiMe}_3$ ), 1.0 ( $\text{SiMe}_2$ ), -8.1, -10.2 ( $\text{SiMe}$ ). -  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz):  $\delta$  30.4 ( $\text{SiMe}_2\text{Cl}$ ), -11.4, -11.7 ( $\text{SiMe}_3$ ), -31.3 ( $\text{SiMe}_2$ ), -70.6, -80.3 ( $\text{SiMe}$ ).  $\text{C}_{21}\text{H}_{63}\text{ClSi}_{10}$  (632.03): calcd. C 39.91, H 10.05; found C 39.25, H 10.00.



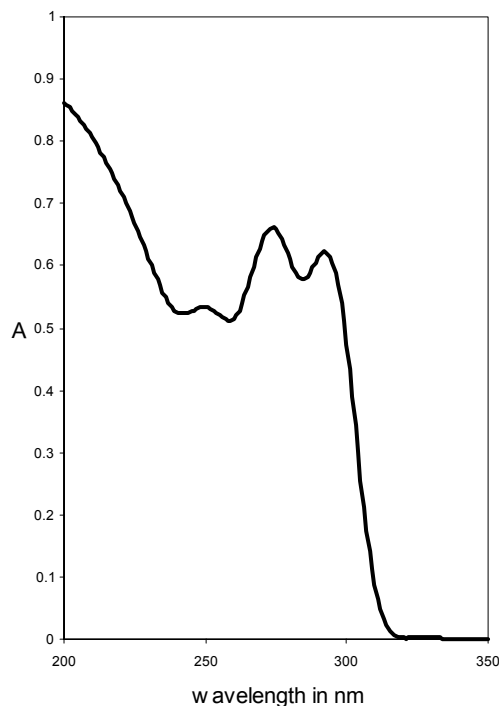
*1,1,1,2,3,3,4,5,5,6,6,7,8,8,9,10,10,10-Octadecamethyl-2,9-bis(trimethylsilyl)-4,7-bis[1',1',2',3',3',3'-hexamethyl-2'-trimethylsilyl-trisilanyl]decasilane (4):*

A suspension of Na-K-alloy (0.164 g, 4.57 mmol; Na/K = 1/4),  $\text{ClMe}_2\text{SiSi}[\text{SiMe}_2\text{Si}(\text{SiMe}_3)_2\text{Me}]_2\text{Me}$  (2.88 g, 4.56 mmol) and n-heptane (20 ml) was stirred at  $100^{\circ}\text{C}$  for two days. After cooling to room temperature, the mixture was filtered off and all volatiles were removed under vacuum. The remaining raw product was suspended in acetone, filtered off and recrystallized from ethyl acetate to give 0.843 g (31 %) of **4**. - Mp.  $173^{\circ}\text{C}$ . -  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 250 MHz):  $\delta$  0.67 (s,  $\text{SiMe}$ , 6 H), 0.66, 0.62, 0.58 (3s,  $\text{SiMe}_2$ ,  $3 \times 12$  H), 0.40 (s,  $\text{SiMe}$ , 12 H), 0.30, 0.29 (2s,  $\text{SiMe}_3$ ,  $2 \times 36$  H). -  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 62.9 MHz):  $\delta$  2.1, 1.9, 0.6 ( $\text{SiMe}_2$ ), 1.2, 1.1 ( $\text{SiMe}_3$ ), -5.6, -9.8 ( $\text{SiMe}$ ). -  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz):  $\delta$  -11.3, -11.4 ( $\text{SiMe}_3$ ), -30.0, -31.7 ( $\text{SiMe}_2$ ), -64.6, -80.0 ( $\text{SiMe}$ ). - MS (CI, isobutane):  $m/z$  (%) = 943 (8) [ $\text{M}^+$ - $\text{SiMe}_2\text{Si}(\text{SiMe}_3)_2\text{Me}$ ]; 653 (55) [ $\text{SiMe}_2\text{SiMe}_2\text{Si}[\text{SiMe}_2\text{Si}(\text{SiMe}_3)_2\text{Me}]_2\text{Me}^+$ ], 595 (43) [ $\text{SiMe}_2\text{Si}[\text{SiMe}_2\text{Si}(\text{SiMe}_3)_2\text{Me}]_2\text{Me}^+$ ]. -  $\text{C}_{42}\text{H}_{126}\text{Si}_{20}$  (1193.19): calcd. C 42.28, H 10.64; found C 40.81, H 10.64.

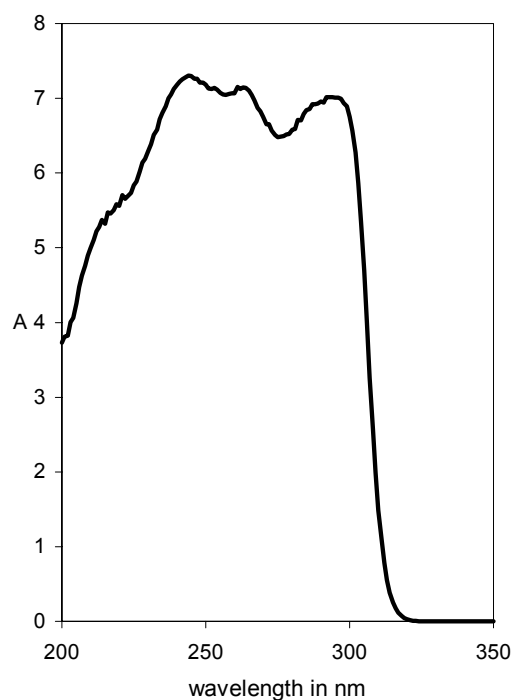


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UV spectrum (thin film)



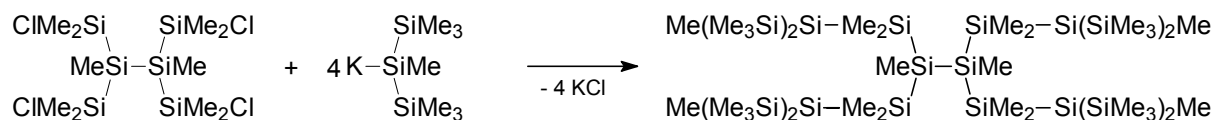
UV spectrum (solid state)



*1,1,1,2,3,3,4,5,6,6,7,8,8,8-Tetradecamethyl-2,7-bis(trimethylsilyl)-4,5-bis[1',1',2',3',3',3'-hexamethyl-2'-trimethylsilyl-trisilanyl]octasilane (5):*

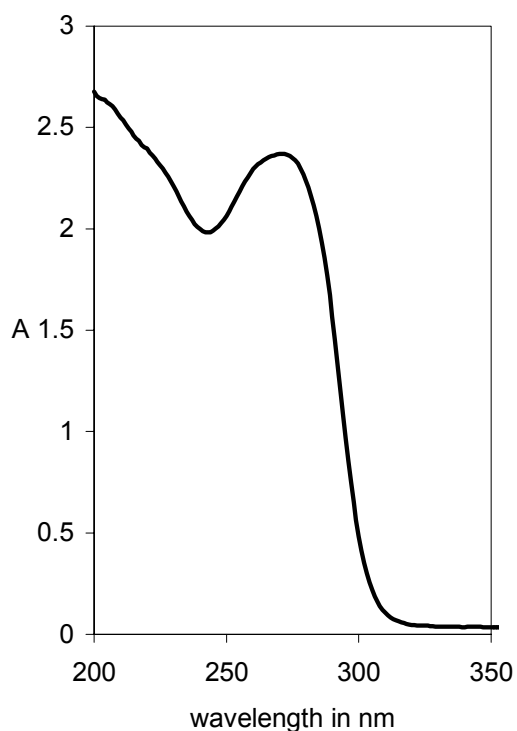
In a Schlenk flask with magnetic stirrer were placed rapidly  $\text{MeSi}(\text{SiMe}_3)_3$  (710 mg, 2.7 mmol) and  $\text{Bu}^t\text{OK}$  (61 mg, 2.7 mmol). The flask was evaporated and refilled with argon three times, THF (40 mL) was added and the yellow solution of  $\text{K-Si}(\text{SiMe}_3)_2\text{Me}$  immediately formed was stirred overnight. After removal of the solvent and other volatiles under vacuum, the remaining solid was dissolved in pentane, the stirred solution cooled to  $-78^\circ\text{C}$  and a pentane solution of  $(\text{ClMe}_2\text{Si})_2\text{SiMe-SiMe}(\text{SiMe}_2\text{Cl})_2$  (250 mg, 0.54 mmol) was added. Stirring was continued for 30 min at  $-78^\circ\text{C}$  and the mixture was allowed to warm up to room temperature within 2 hours. After filtration and removal of the solvent, the residue was kept under high vacuum at  $100^\circ\text{C}$  to remove volatile by-products and recrystallized from acetone to give 415 mg of **5** (71%). - Mp.  $148^\circ\text{C}$ . -  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 250 MHz):  $\delta$  0.81 (s, SiMe, 6 H),

2 × 0.65 (2s, SiMe<sub>2</sub>, 2 × 12 H), 0.45 (s, SiMe, 12 H), 2 × 0.3 (2s, SiMe<sub>3</sub>, 2 × 18 H). - <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 62.9 MHz): δ 3.4, 2.4 (SiMe<sub>2</sub>), 1.6, 1.4 (SiMe<sub>3</sub>), -1.8, -9.0 (SiMe). - <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 59.6 MHz): δ -11.1, -11.3 (SiMe<sub>3</sub>), -28.6 (SiMe<sub>2</sub>), -55.1, -77.9 (SiMe). - MS (CI, isobutane): *m/z* (%) = 1059 (28) [M<sup>+</sup>-Me]; 827 (50) [M<sup>+</sup>-SiMe<sub>2</sub>Si(SiMe<sub>3</sub>)<sub>2</sub>Me], 537 (71) [Si[SiMe<sub>2</sub>Si(SiMe<sub>3</sub>)<sub>2</sub>Me]<sub>2</sub>Me<sup>+</sup>]. - C<sub>38</sub>H<sub>114</sub>Si<sub>18</sub> (1076.86): calcd. C, 42.38, H, 10.67; found C, 41.30, H, 10.73.

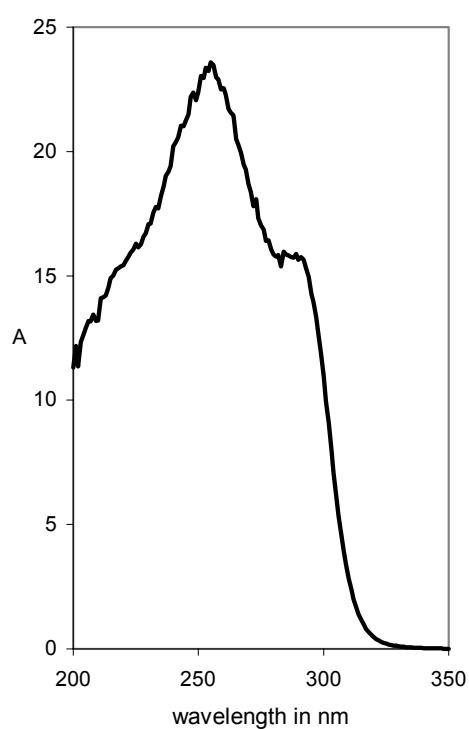


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UV spectrum (thin film)



UV spectrum (solid state)



## References

- [1] U. Herzog, N. Schulze, K. Trommer, and G. Roewer, *J. Organomet. Chem.* 1997, **547**, 133-139.
- [2] G. Kollegger and K. Hassler, *J. Organomet. Chem.* 1995, **485**, 233-236.

## X-ray Crystallography

*Crystal data:* 1,1,1,2,3,3,4,5,6,6,7,8,8,8-Tetradecamethyl-2,7-bis(trimethylsilyl)-4,5-bis[1',1',2',3',3',3'-hexamethyl-2'-trimethylsilyl-trisilanyl]octasilane (**4**): CCDC 275783: A small white crystal was mounted on top of a thin glass fiber. Intensity data of this crystal were collected at room temperature using graphite monochromatized Mo K $\alpha$ -radiation on a Bruker-Nonius APEX-II-CCD-diffractometer. C<sub>38</sub>H<sub>114</sub>Si<sub>18</sub>, M = 1076.86: monoclinic, C2/c (no. 15),  $a = 23.2800(7)$  Å,  $b = 17.9532(6)$  Å,  $c = 17.7010(5)$  Å,  $\beta = 94.237(1)^\circ$ ,  $V = 7377.9(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 0.970$  g·cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 3.3$  cm<sup>-1</sup>, total reflections 46850, independent reflections 8127 ( $R_{\text{int}} = 0.080$ ), refinements on  $F^2$ ,  $R1 = 0.0473$ ,  $wR2 = 0.1090$ . See <http://www.rsc.org/suppdata/cc???????> for crystallographic data in cif or other electronic format.

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