

Supporting information for

Alkylated Cage Silsesquioxanes: A Comprehensive Study of Thermal Property and Self-Assembled Structure

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1. Experimental section

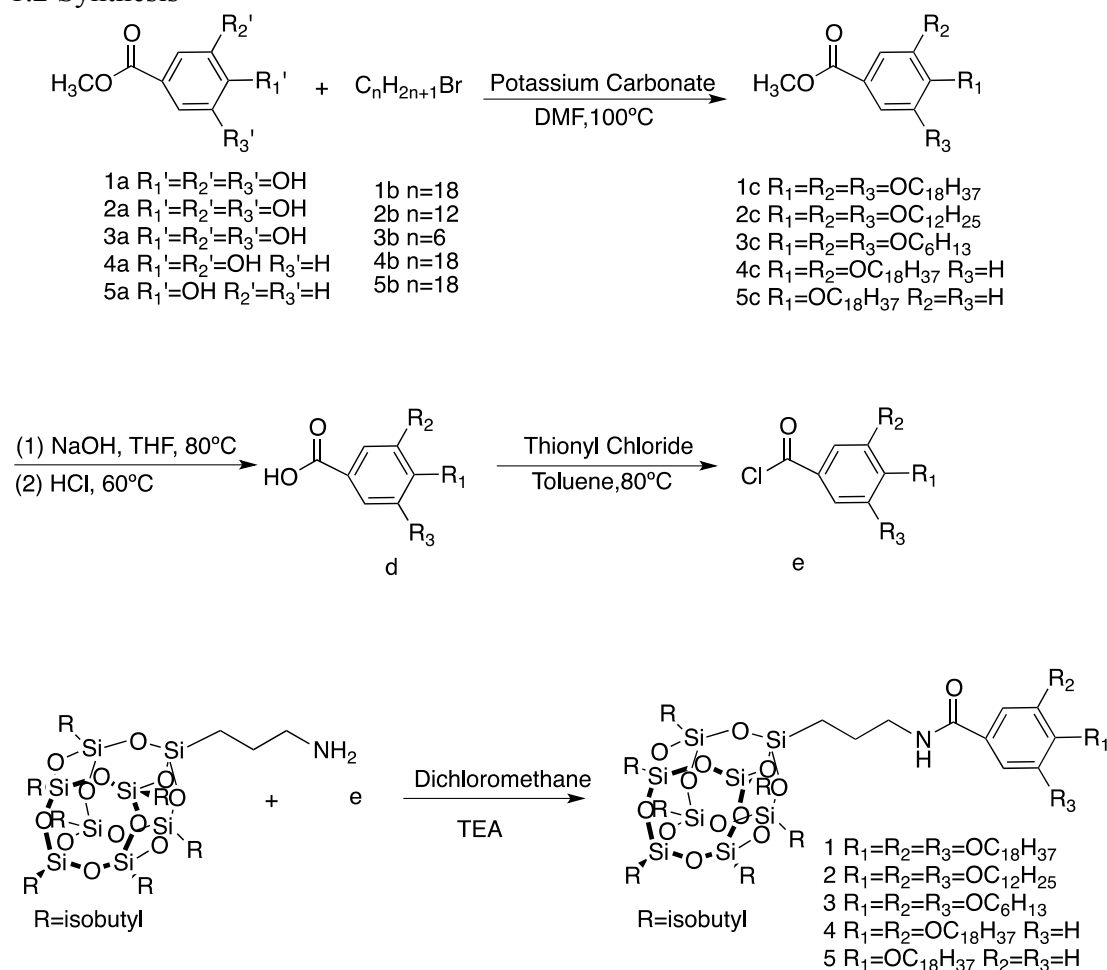
1.1 Materials and methods

Aminopropylisobutyl POSS was purchased from Hybrid Plastics. All other reagents used were purchased from Tokyo Chemical Industry (TCI), Sigma Aldrich or Wako, and were used without further purification.

Recycling preparative size exclusion chromatography (SEC) was performed using JAIGEL 2H and 3H columns on a JAL model LC-9204 high-performance liquid chromatograph (HPLC) equipped with a UV/VIS detector (UV-3740) and RI detector (RI-50S). Nuclear magnetic resonance (NMR) spectra recorded using a JEOL 400 MHz with chloroform-*d* as the solvent; a ¹H: 7.26 solvent signal was used as an internal standard for all chemical shifts. Similarly, for the ¹³C NMR spectra, a signal consistent with chloroform-*d* (77.2 ppm) was used as an internal reference. IR spectra were recorded on a JASCO FT/IR-4100 plus spectrophotometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu AXIMA-performance mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm) and pulsed ion extraction, which was operated in a linear-positive ion mode at an accelerating potential of 20 kV. Tetrahydrofuran (THF) solutions containing 1 g/L of sample, 10 g/L of dithranol, and 1 g/L of sodium trifluoroacetate were mixed to a ratio of 1:1:1; a 1 μ L aliquot of this mixture was deposited onto a sample target plate. Elemental analysis was performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer. The thermal properties and mesophase structure of alkylated POSS **1** was evaluated at a heating rate of 10 °C /min under a nitrogen flow by a Seiko DSC 7020 differential scanning calorimeter (DSC); the transition temperature values were determined from the second heating and cooling scan. Microscopic observation of thermal events was also conducted using an Olympus

BH-2 polarized optical microscope equipped with a Mettler FP82HT hot-stage system. To determine the temperature-dependent aggregation of the alkylated POSS, wide-angle X-ray scattering (WAXS) patterns were obtained using an imaging plate (IP) film and IP detector (R-AXIS, DS3C, Rigaku Co.). These IP films were attached to a Bruker AXS K.K X-ray generator (Cu K α , wavelength = 0.154 nm) operated at 50 kV and 100 mA. The sample was exposed to the X-ray beam for 15 min, with a sample-to-film distance of 109 mm. The resulting WAXS pattern was used to determine the *d*-spacing using specialized software for data analysis (RIGAKU R-AXIS, Rigaku Co.). Bright field transmission electron microscope (TEM) images of the sample structure were also obtained using a Hitachi H7650 Zero A under an 80 KV accelerating voltage. Bulk samples were prepared for TEM analysis by first being pasted onto epoxy resin for handling, then microtomed (Reichert-Jung Ultracut E) by a DiATOME diamond knife at room temperature to a preset thickness of 70 nm. The sections produced were then placed onto TEM grids and stained by ruthenium oxide for observation.

1.2 Synthesis



Scheme 1. Synthesis route for alkylated POSS 1-5

1.2.1 General synthetic procedure of 1c-5c

Gallic acid methyl ester (2.76 g, 15 mmol) and bromoalkane (54 mmol) were added to a suspension of potassium carbonate (18.65 g, 135 mmol) in DMF (75 ml), and then stirred at 90°C for 48 h. This mixture was then poured into cold water, and the resulting suspension was extracted with chloroform. Following this, the combined organic phase was washed with water and dried by anhydrous magnesium, the desiccating agent then removed by filtration and concentrated under reduced pressure. Finally, a column of silica gel with chloroform as an eluent was used to purify the crude product.

Methyl 3,4,5-Tris (octadecyloxy) benzoate (**1c**) Yield: 80%. ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, 9H, 3CH_3), 1.25 (broad, 84H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.44 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.81 (m, 6H, OCH_2CH_2), 3.89 (s, 3H, OCH_3), 4.00 (t, 6H, OCH_2), 7.25 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 25.7, 29.4, 31.9, 52.0, 69.3, 73.5, 107.9, 124.7, 142.3, 152.8, 167.0. IR (KBr, cm^{-1}): 2921, 2849, 1714, 1539, 1507, 1475, 1344, 1232, 1129, 993, 909, 862, 767, 722. Elemental analysis: calcd. (%) for $\text{C}_{62}\text{H}_{116}\text{O}_5$, C 79.09; H 12.42. found (%) C 78.96; H 12.69.

Methyl 3,4,5-Tris (dodecyloxy) benzoate (**2c**) Yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, 9H, 3CH_3), 1.25 (broad, 48H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$), 1.43 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.78 (m, 6H, OCH_2CH_2), 3.86(s, 3H, OCH_3), 3.99 (t, 6H, OCH_2), 7.23 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 29.6, 31.9, 52.1, 69.1, 107.9, 124.6, 142.3, 152.8, 166.9. Elemental analysis: calcd. (%) for $\text{C}_{44}\text{H}_{80}\text{O}_5$, C 76.69; H 11.70. found (%) C 77.03; H 11.59.

Methyl 3,4,5-Tris (hexyloxy) benzoate (**3c**) Yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, 9H, 3CH_3), 1.29 (broad, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$), 1.43 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.76 (m, 6H, OCH_2CH_2), 4.06 (s, 3H, OCH_3), 3.89 (t, 6H, OCH_2), 7.23 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 25.6, 29.6, 51.5, 69.0, 109.4, 124.9, 153.5, 165.9. Elemental analysis: calcd. (%) for $\text{C}_{26}\text{H}_{44}\text{O}_5$, C 71.52; H 10.16. found (%) C 71.56; H 10.32.

Methyl 3,4-Bis (octadecyloxy) benzoate (**4c**) Yield: 75%. ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, 6H, 2CH_3), 1.28 (broad, 56H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.43 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.79 (m, 4H, OCH_2CH_2), 3.86(s, 3H, OCH_3), 3.99 (t, 4H, OCH_2), 7.14 (b, H, ArH), 7.50(b, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 25.9, 29.6, 31.9, 51.9, 69.0, 111.9, 114.4, 122.4, 153.5, 166.9. Elemental analysis: calcd. (%) for $\text{C}_{44}\text{H}_{80}\text{O}_4$, C 78.51; H 11.98. found (%) C 78.34; H 12.02.

Methyl 4-octadecyloxy benzoate (**5c**) Yield: 84%. ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, 3H, CH_3), 1.29 (broad, 28H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.42 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.78 (m, 2H, OCH_2CH_2), 3.89(s, 3H, OCH_3), 3.99 (t, 2H, OCH_2), 6.86 (b, 2H, ArH), 7.94 (b, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 25.9, 29.3, 29.6, 31.9, 51.8, 68.2, 114.0, 122.3, 131.5, 162.9, 166.9. Elemental analysis: calcd. (%) for $\text{C}_{26}\text{H}_{44}\text{O}_3$, C 77.18; H 10.96. found (%) C 77.50; H 10.65.

1.2.2 General synthetic procedure of **1d-5d**

To a mixture of **c** (12.0 mmol) and THF (480 ml), a solution of sodium hydroxide (4.80g, 120 mmol) in water (72.0 ml) was added, then refluxed for 48 hours. Concentrated hydrochloric acid (48 ml) was added to this solution, and then stirred for 5 hours at 50 °C. Separatory funnel was used to separate organic phase. Then, anhydrous magnesium sulfate was used to dry organic phase. The product can be obtained by the removal of THF by using a rotary evaporator.

3,4,5-Tris(octadecyloxy)benzoyl acid (**1d**) Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, 9H, 3 CH_3), 1.26-1.31 (broad, 84H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.45 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.77 (m, 6H, OCH_2CH_2), 4.01 (t, 6H, OCH_2), 7.21 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.8, 26.2, 29.4, 29.5, 31.9, 69.3, 73.6, 108.4, 123.8, 142.9, 152.8. IR (KBr, cm^{-1}): 2921, 2489, 1690, 1587, 1511, 1471, 1432, 1380, 1335, 1228, 1125, 1053, 866, 711. Elemental analysis: calcd. (%) for $\text{C}_{61}\text{H}_{116}\text{O}_5$, C 78.99; H 12.39. found (%) C 78.72; H 12.43.

3,4,5-Tris(dodecyloxy)benzoyl acid (**2d**) Yield: 93%. ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, 9H, 3 CH_3), 1.24 (broad, 48H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$), 1.46 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.77 (m, 6H, OCH_2CH_2), 4.02 (t, 6H, OCH_2), 7.23 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 29.4, 31.9, 69.2, 108.5, 123.5, 143.1, 152.8,

171.6. . Elemental analysis: calcd. (%) for C₄₄H₇₈O₆, C 75.15; H 11.18. found (%) C 75.42; H 11.40.

3,4,5-Tris(hexyloxy)benzoyl acid (**3d**) Yield: 91%. ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, 9H, 3CH₃), 1.29 (broad, 12H, OCH₂CH₂CH₂-(CH₂)₂-CH₃), 1.43 (m, 6H, OCH₂CH₂CH₂), 1.77 (m, 6H, OCH₂CH₂), 4.04 (t, 6H, OCH₂), 7.23 (s, 2H, ArH). ¹³C NMR (400 MHz, CDCl₃) δ 14.1, 22.6, 25.7, 69.1, 108.5, 123.6, 143.1, 152.8, 171.7. Elemental analysis: calcd. (%) for C₂₆H₄₂O₆, C 69.30; H 9.39. found (%) C 69.51; H 9.24.

3,4-Bis (octadecyloxy) benzoyl acid (**4d**) Yield: 91%. ¹H NMR (400 MHz, CDCl₃) δ 0.86 (t, 6H, 2CH₃), 1.29 (broad, 56H, OCH₂CH₂CH₂-(CH₂)₁₄-CH₃), 1.43 (m, 4H, OCH₂CH₂CH₂), 1.77 (m, 4H, OCH₂CH₂), 4.02 (t, 6H, OCH₂), 7.11 (b, H, ArH), 7.50(b, H, ArH), 7.60(b, H, ArH). ¹³C NMR (400 MHz, CDCl₃) δ 14.1, 22.7, 26.0, 29.4, 29.6, 31.9, 69.0, 111.9, 114.1, 122.3, 153.1, 167.0. Elemental analysis: calcd. (%) for C₄₄H₇₈O₅, C 76.91; H 11.44. found (%) C 76.52; H 11.52.

Methyl 4-octadecyloxybenzoyl acid (**5d**) Yield: 91%. ¹H NMR (400 MHz, CDCl₃) δ 0.86 (t, 3H, CH₃), 1.29 (broad, 28H, OCH₂CH₂CH₂-(CH₂)₁₄-CH₃), 1.43 (m, 2H, OCH₂CH₂CH₂), 1.78 (m, 2H, OCH₂CH₂), 4.12 (t, 2H, OCH₂), 6.91 (b, 2H, ArH), 7.99 (b, 2H, ArH). ¹³C NMR (400 MHz, CDCl₃) δ 14.1, 22.6, 29.6, 67.7, 114.6, 121.8, 131.6, 160.7, 164.6, 169.3. Elemental analysis: calcd. (%) for C₂₆H₄₂O₄, C 74.60; H 10.11. found (%) C 74.41; H 10.48.

1.2.3 General synthetic procedure of **1e-5e**

To a 300ml round-bottomed flask, **d** (12 mmol), 150 ml toluene and 40 ml thionyl chloride were added. The mixture was stirred at 80 °C for 24 hours. Then, thionyl chloride and toluene were evaporated under vacuum. The remaining thionyl chloride

and toluene were removed under reduced pressure distillation. The raw product can be further purified by recrystallization in hexane.

3,4,5-Tris(octadecyloxy)benzoyl chloride (**1e**) Yield: 86%. ^1H NMR (400 MHz, CDCl_3) δ 0.90 (t, 9H, 3CH_3), 1.26-1.31 (broad, 84H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.44 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.84 (m, 6H, OCH_2CH_2), 4.06 (t, 6H, OCH_2), 7.32 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.2, 22.8, 26.1, 29.3, 29.6, 32.0, 69.4, 73.8, 110.0, 127.3, 145.3, 152.9, 167.8. IR (KBr, cm^{-1}): 2960, 2916, 2853, 1754, 1587, 1507, 1468, 1436, 1388, 1335, 1240, 1152, 1125, 1025, 973, 876, 862, 806, 767, 715, 694, 607. Elemental analysis: calcd. (%) for $\text{C}_{61}\text{H}_{113}\text{ClO}_4$, C 77.45; H 12.04. found (%) C 77.16; H 12.67.

3,4,5-Tris(dodecyloxy)benzoyl chloride (**2e**) Yield: 83%. ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, 9H, 3CH_3), 1.26-1.31 (broad, 48H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$), 1.45 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.77 (m, 6H, OCH_2CH_2), 4.00 (t, 6H, OCH_2), 7.23 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 29.4, 31.9, 69.1, 108.5, 123.5, 143.2, 152.8, 171.0. Elemental analysis: calcd. (%) for $\text{C}_{43}\text{H}_{77}\text{ClO}_4$, C 74.47; H 11.19. found (%) C 74.26; H 11.31.

3,4,5-Tris(hexyloxy)benzoyl chloride (**3e**) Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, 9H, 3CH_3), 1.29-1.32 (broad, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$), 1.45 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.76 (m, 6H, OCH_2CH_2), 4.05 (t, 6H, OCH_2), 7.13 (s, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.0, 22.6, 25.7, 29.3, 31.7, 69.1, 107.9, 126.5, 144.6, 152.8, 167.6. Elemental analysis: calcd. (%) for $\text{C}_{25}\text{H}_{41}\text{ClO}_4$, C 68.08; H 9.37. found (%) C 67.89; H 9.32.

3,4-bis(octadecyloxy) benzoyl chloride (**4e**) Yield: 91%. ^1H NMR (400 MHz, CDCl_3) δ 0.81 (t, 6H, 2CH_3), 1.25 (broad, 56H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.40 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.76 (m, 4H, OCH_2CH_2), 3.98 (t, 6H, OCH_2), 7.46 (b, H, ArH),

7.57(b, H, ArH), 7.71(b, H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 25.9, 29.4, 29.6, 31.9, 51.9, 69.0, 111.9, 122.3, 125.4, 148.6, 153.0, 166.9. Elemental analysis: calcd. (%) for $\text{C}_{43}\text{H}_{77}\text{ClO}_3$, C 76.23; H 11.46. found (%) C 76.35; H 11.72.

Methyl 4-octadecyloxybenzoyl chloride (**5e**) Yield: 91%. ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, 3H, CH_3), 1.29 (broad, 28H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.41 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.77 (m, 2H, OCH_2CH_2), 4.00 (t, 2H, OCH_2), 6.91 (b, 2H, ArH), 8.02 (b, 2H, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 14.1, 22.7, 25.9, 29.6, 31.9, 51.9, 68.2, 114.6, 122.3, 131.5, 162.9, 166.9. Elemental analysis: calcd. (%) for $\text{C}_{25}\text{H}_{41}\text{ClO}_2$, C 73.41; H 10.10. found (%) C 73.39; H 10.15.

1.2.4 General synthetic procedure of **1-5**

0.26 g (0.3 mmol) aminopropylisobutyl POSS, 0.36 mmol **e** and 10ml dichloromethane were added into 20 ml round-bottomed flask. Then, 0.5 ml triethylamine was added into the solution. The mixture was stirred at room temperature for 3 hours. After that, 10 ml deionized water was added to remove the triethylamine hydrochloride. Separatory funnel was used to separate organic phase. Then, anhydrous MgSO_4 was used to dry organic phase. The raw product can be obtained by the removal of THF by using a rotary evaporator. Recycling preparative HPLC was employed to get purified product.

Alkylated POSS (**1**) Yield: 65%. ^1H NMR (400 MHz, CDCl_3) δ 0.57(b, 14H, Si-CH_2), 0.86 (broad, 11H, overlapped, SiCH_2CH_2 and CH_2CH_3), 0.93 (b, 42H, $\text{CH}(\text{CH}_3)_2$), 1.24-1.28 (broad, 84H, $\text{OCH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2)_{14}-\text{CH}_3$), 1.44 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.78 (broad, 13H, overlapped, OCH_2CH_2 and $\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 3.39 (m, 1H, $\text{SiCH}_2\text{CH}_2\text{NH}$), 3.97 (m, 6H, OCH_2), 6.91 (s, ArH). ^{13}C NMR (400 MHz, CDCl_3) δ 9.7, 14.1, 22.9, 25.7, 29.7, 32.1, 69.4, 73.6, 105.7, 130.1, 141.1, 153.1, 167.5. IR (KBr, cm^{-1}): 2952, 2924, 2849, 1634, 1587, 1542, 1471, 1427, 1335, 1236,

1112, 841, 742, 567, 484. MALDI-TOF MS m/z calc for $C_{92}H_{184}NO_{16}Si_8$ $[M+H^+]$ 1784.45; found 1784.67. Elemental analysis: calcd. (%) for $C_{92}H_{183}NO_{16}Si_8$, C 61.93; H 10.36; N 0.78. found (%) C 61.70; H 10.69; N 0.76.

Alkylated POSS (2) Yield: 65%. 1H NMR (400 MHz, $CDCl_3$) δ 0.57(b, 14H, Si- CH_2), 0.86 (broad, 8H, overlapped, Si CH_2CH_2 and CH_2CH_3), 0.93 (b, 42H, $CH(CH_3)_2$), 1.24 (broad, 48H, $OCH_2CH_2CH_2-(CH_2)_8-CH_3$), 1.44(m, 6H, $OCH_2CH_2CH_2$), 1.78 (broad, 13H, overlapped, OCH_2CH_2 and Si $CH_2CH(CH_3)_2$), 3.39(m, 1H, Si CH_2CH_2NH), 3.99(m, 6H, OCH_2), 6.91 (s, ArH). MALDI-TOF MS m/z calc for $C_{74}H_{148}NO_{16}Si_8$ $[M+H^+]$ 1532.17; found 1532.48. Elemental analysis: calcd. (%) for $C_{74}H_{147}NO_{16}Si_8$, C 58.04; H 9.69; N 0.91. found (%) C 58.23; H 9.51; N 0.88.

Alkylated POSS (3) Yield: 63%. 1H NMR (400 MHz, $CDCl_3$) δ 0.57(b, 14H, Si- CH_2), 0.88 (broad, 8H, overlapped, Si CH_2CH_2 and CH_2CH_3), 0.94 (b, 42H, $CH(CH_3)_2$), 1.28 (broad, 12H, $OCH_2CH_2CH_2-(CH_2)_2-CH_3$), 1.44(m, 6H, $OCH_2CH_2CH_2$), 1.78 (broad, 13H, overlapped, OCH_2CH_2 and Si $CH_2CH(CH_3)_2$), 3.39(m, 1H, Si CH_2CH_2NH), 3.98(m, 6H, OCH_2), 6.91 (s, ArH). ^{13}C NMR (400 MHz, $CDCl_3$) δ 9.6, 14.1, 22.6, 25.7, 29.3, 31.5, 69.4, 77.0, 105.7, 130.2, 141.1, 153.0, 167.1. MALDI-TOF MS m/z calc for $C_{56}H_{112}NO_{16}Si_8$ $[M+H^+]$ 1279.40; found 1280.37. Elemental analysis: calcd. (%) for $C_{56}H_{111}NO_{16}Si_8$, C 52.61; H 8.77; N 1.10. found (%) C 52.87; H 8.53; N 1.04.

Alkylated POSS (4) Yield: 70%. 1H NMR (400 MHz, $CDCl_3$) δ 0.57(b, 14H, Si- CH_2), 0.88 (broad, 8H, overlapped, Si CH_2CH_2 and CH_2CH_3), 0.94 (b, 42H, $CH(CH_3)_2$), 1.28 (broad, 56H, $OCH_2CH_2CH_2-(CH_2)_{14}-CH_3$), 1.44(m, 4H, $OCH_2CH_2CH_2$), 1.78 (broad, 11H, overlapped, OCH_2CH_2 and Si $CH_2CH(CH_3)_2$), 3.39(m, 2H, Si CH_2CH_2NH), 3.98(m, 4H, OCH_2), 6.91 (s, ArH). ^{13}C NMR (400

MHZ, CDCl₃) δ 9.6, 14.1, 22.7, 25.7, 29.4, 31.9, 69.3, 105.7, 112.1, 119.1, 127.4, 149.0, 167.1. MALDI-TOF MS m/z calc for C₇₄H₁₄₈NO₁₅Si₈ [M+H⁺] 1515.18; found 1516.43. Elemental analysis: calcd. (%) for C₇₄H₁₄₇NO₁₅Si₈, C 58.66; H 9.80; N 0.92. found (%) C 58.95; H 9.61; N 0.96.

Alkylated POSS (**5**) Yield: 69%. ¹H NMR (400 MHz, CDCl₃) δ 0.57(b, 14H, Si-CH₂), 0.88 (broad, 5H, overlapped, SiCH₂CH₂ and CH₂CH₃), 0.94 (b, 42H, CH(CH₃)₂), 1.28 (broad, 28H, OCH₂CH₂CH₂-(CH₂)₁₄-CH₃), 1.44(m, 2H, OCH₂CH₂CH₂), 1.78 (broad, 9H, overlapped, OCH₂CH₂ and SiCH₂CH(CH₃)₂), 3.39(m, 2H, SiCH₂CH₂NH), 3.98(m, 2H, OCH₂), 6.91 (s, ArH). ¹³C NMR (400 MHz, CDCl₃) δ 9.3, 14.1, 22.7, 25.7, 29.4, 31.9, 67.8, 114.2, 126.6, 161.7, 167.1. MALDI-TOF MS m/z calc for C₅₆H₁₁₂NO₁₄Si₈ [M+H⁺] 1247.90; found 1248.25. Elemental analysis: calcd. (%) for C₅₆H₁₁₁NO₁₄Si₈, C 53.94; H 8.99; N 1.12. found (%) C 53.97; H 9.07; N 1.09.

2. Phase transitions and corresponding enthalpies of alkylated silsesquioxane derivatives

	$T_1/^{\circ}\text{C}$ ($\Delta\text{H}/\text{KJ mol}^{-1}$)	$T_2/^{\circ}\text{C}$ ($\Delta\text{H}/\text{KJ mol}^{-1}$)	$T_3/^{\circ}\text{C}$ ($\Delta\text{H}/\text{KJ mol}^{-1}$)	$T_m/^{\circ}\text{C}$ ($\Delta\text{H}/\text{KJ mol}^{-1}$)
1	69 (1.39)	80 (0.377)	89 (25.9)	133 (48.5)
2	16 (2.28)	25 (9.80)	--	142 (42.6)
3	1 (0.869)	13 (0.805)	--	155 (54.1)
4	71 (0.636)	81 (0.075)	87 (19.9)	128 (36.7)
5	21 (0.822)	64 (1.61)	99 (0.735)	119 (26.2)

Table S1. Phase transitions and corresponding enthalpies of alkylated silsesquioxane derivatives **1-5**.

3. DSC curves of alkylated cage silsesquioxanes **1-5**

3.2 POSS-C₁₈-3A

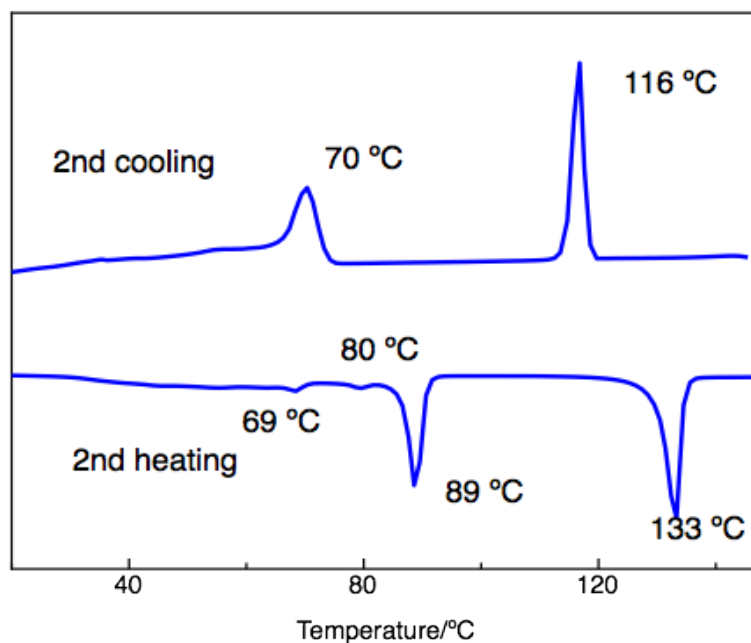


Figure S1. DSC curve of **1** (POSS-C₁₈-3A)

3.2 POSS-C₁₂-3A

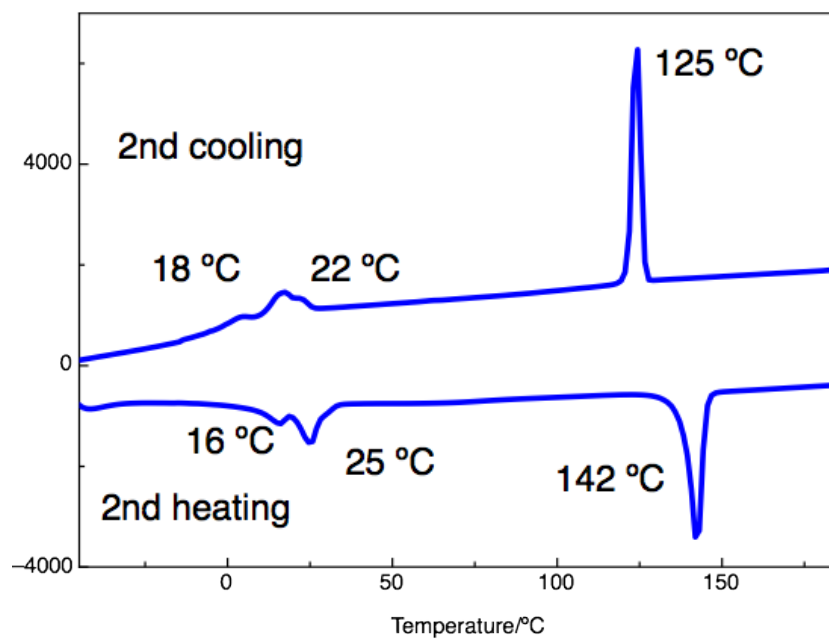


Figure S2. DSC curve of **2** (POSS-C₁₂-3A)

3.3 POSS-C₆-3A

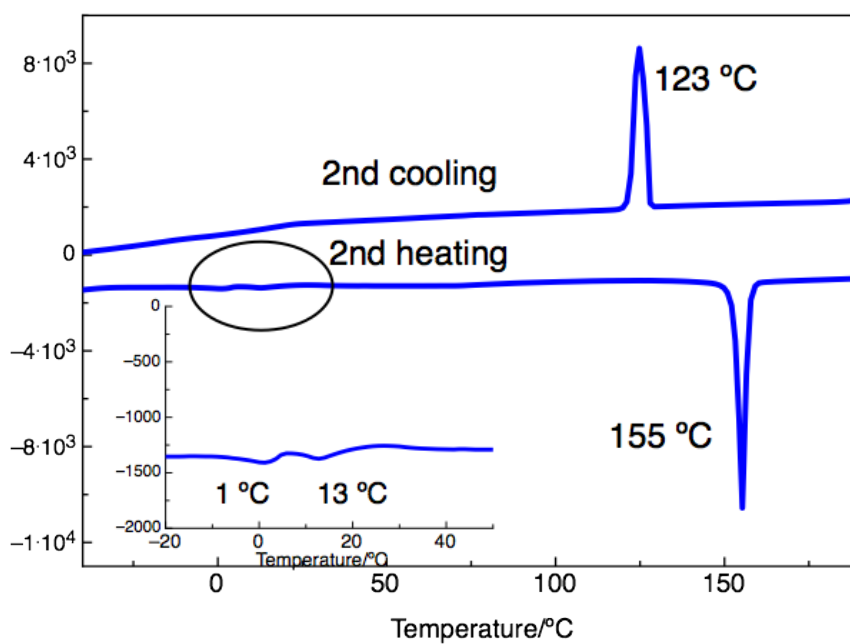


Figure S3. DSC curve of **3** (POSS-C₆-3A)

3.4 POSS-C₁₈-2A

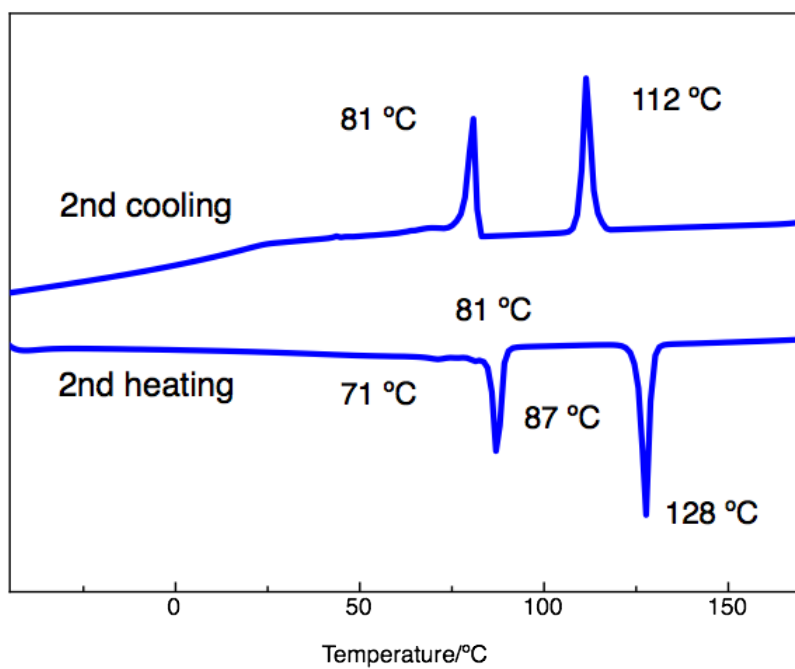


Figure S4. DSC curve of 4 (POSS-C₁₈-2A)

3.5 POSS-C₁₈-1A

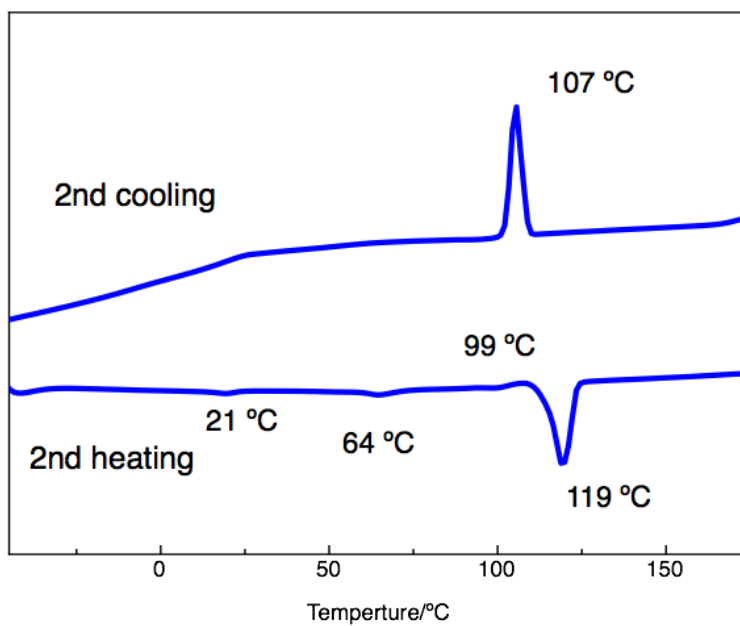


Figure S5. DSC curve of 5 (POSS-C₁₈-1A)

4. POM images of alkylated POSS 2

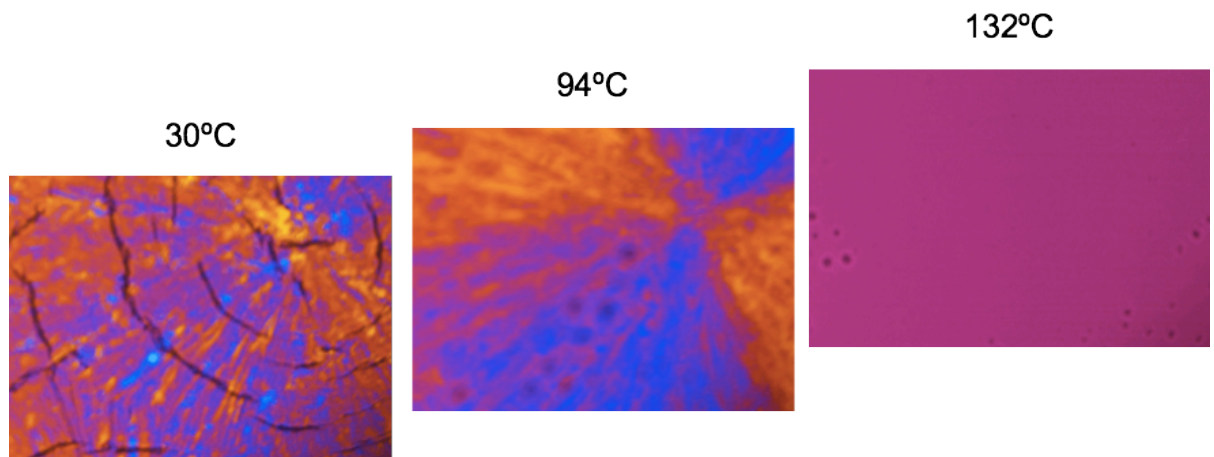


Figure S6: POM images of alkylated POSS 2 under different temperatures.

5. WAXS profiles

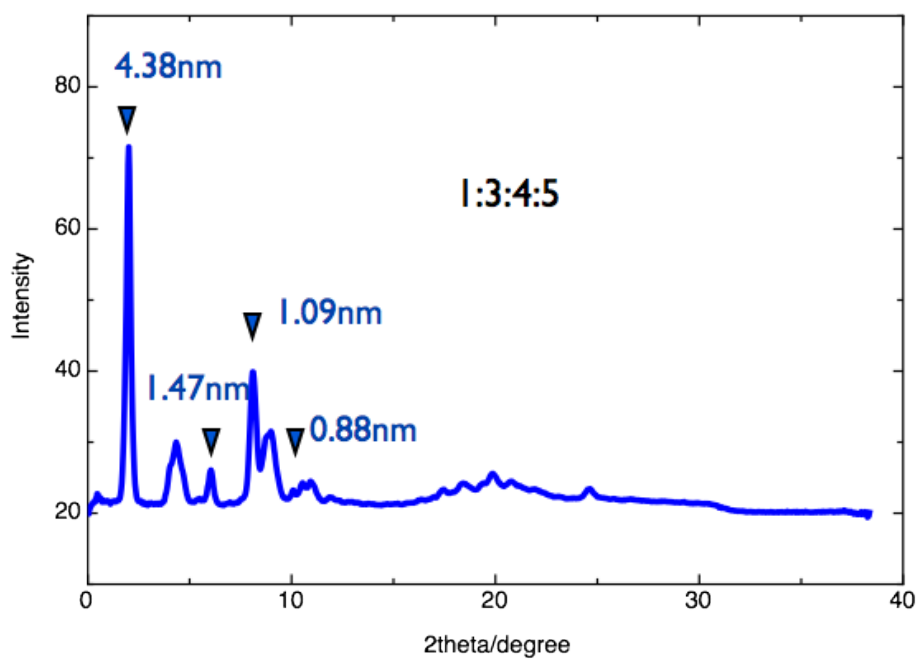


Figure S7. WAXS profile of **2** (POSS-C₁₂-3A)

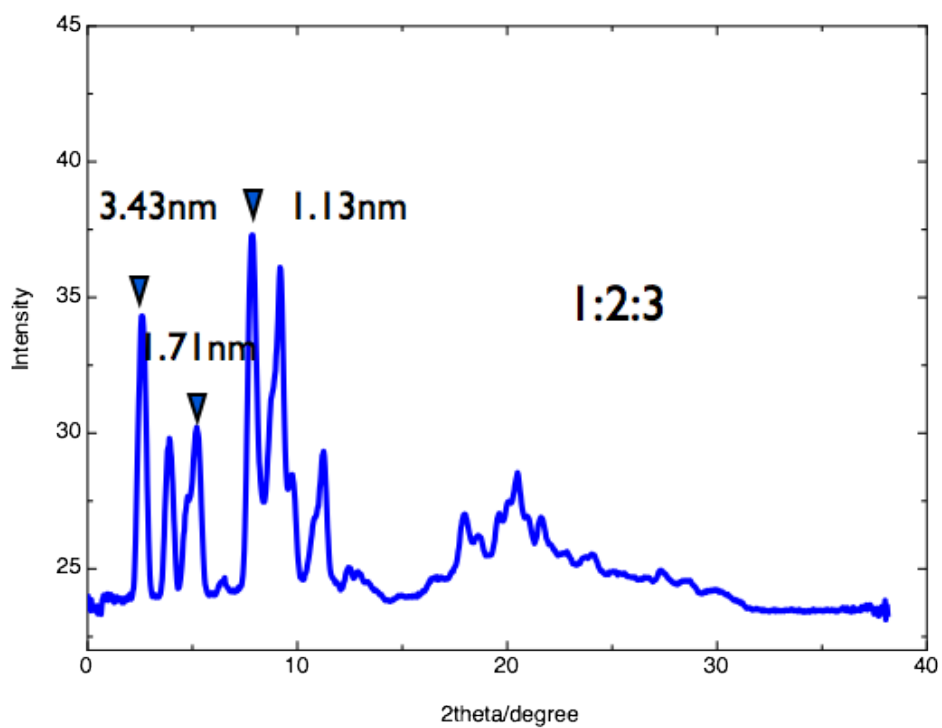


Figure S8. WAXS profile of **3** (POSS-C₆-3A)

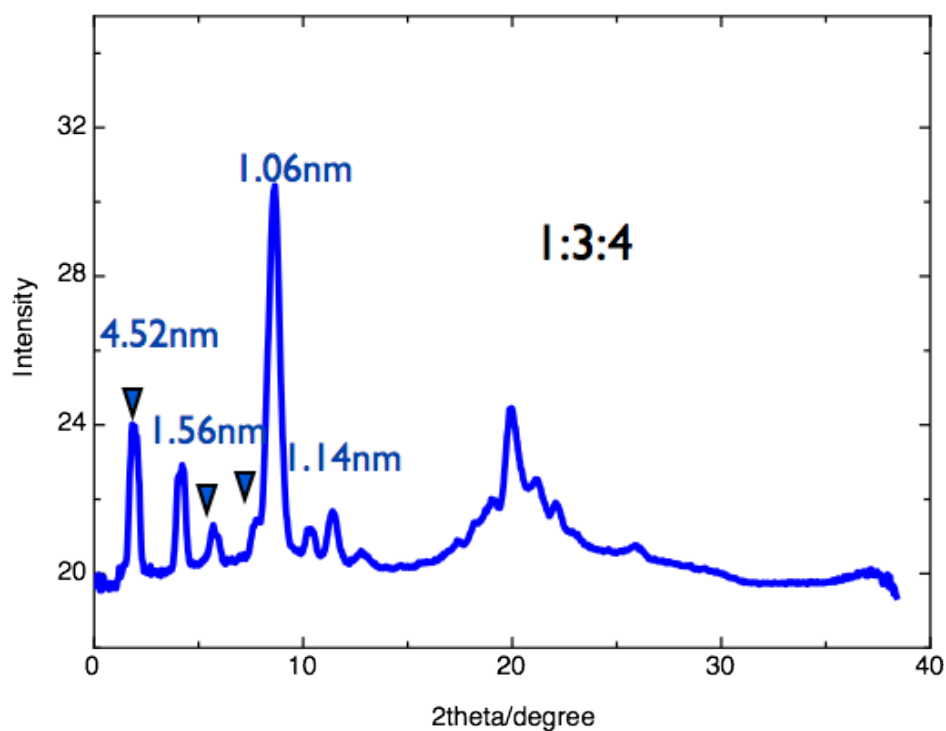


Figure S9. WAXS profile of 4 (POSS-C₁₈-2A)

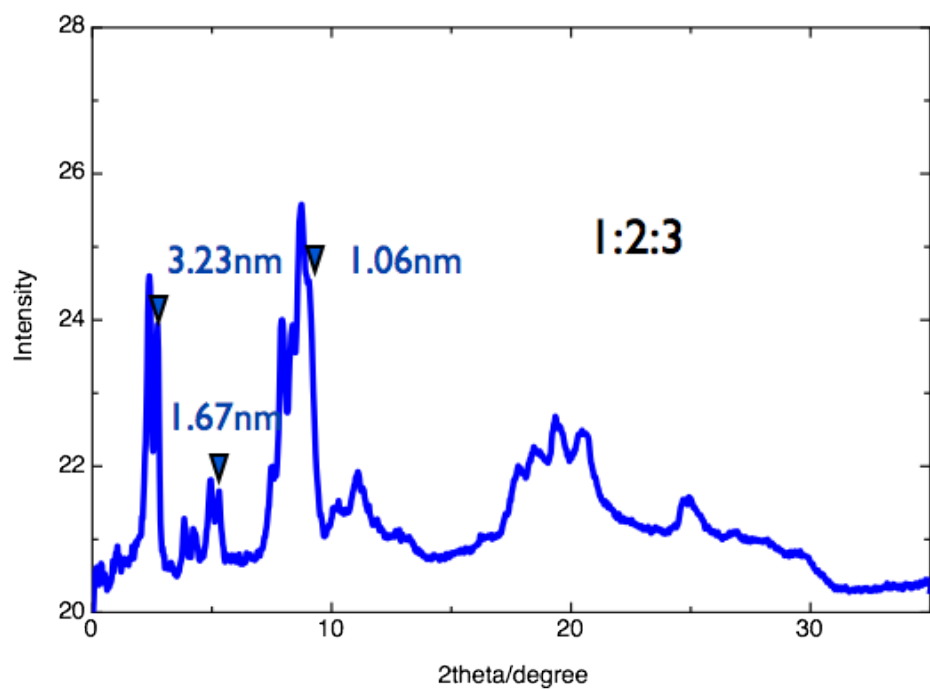


Figure S10. WAXS profile of 5 (POSS-C₁₈-1A)