Supporting Information for

Cooperative Soft-Cluster Glass in Giant Molecular Clusters

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Supporting Text

Materials and Characterizations of synthesis.

Tri-Silanol-Isococyt POSS was purchased from Hybrid Plastics and used as received; size exclusion chromatography (SEC) was performed by Bio-Beads™ S-X Resin; other chemicals and solvents were used as received from Sigma-Aldrich, Acros Organic, or Fisher Scientific.

$^1$H, $^{13}$C and $^{29}$Si NMR experiments were measured on a Varian Mercury 500 M NMR or 300 M NMR spectrometer. $^1$H NMR spectra were referenced to the residual solvent peak in CDCl$_3$ at δ 7.27 ppm and in DMSO-d$_6$ at δ 2.50 ppm, and $^{13}$C NMR spectra were referenced to the residual solvent peak in CDCl$_3$ at δ 77.00 ppm and in DMSO-d$_6$ at δ 39.52 ppm.

Gel permeation chromatography (GPC) were measured in THF at 35 °C on Tosoh EcoSEC instrument with three columns [TSKgel SuperH3000 x 2, TSKgel SuperH5000] with a Guard Column (TSKgel SuperH1000-4000) and a UV detector.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Bruker Ultra flex III TOF/TOF mass spectrometer under reflective mode for small molecules and linear mode for large molecules.

Synthetic Procedures
1. OPOSS-vinyl

To a 500mL round-bottomed flask equipped with a magnetic stirring bar was added trisilanol-isococyt POSS (11.8g, 10 mmol), followed by the addition of 100 mL freshly dried THF to fully dissolve the liquid, TEA (4.6 mL, 33 mmol) was added into the solution, then the flask was capped with a rubber septum and cooled to 0 °C. With stirring, Trichlorovinylsilane (1.4 mL, 11 mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 14 h at room temperature. After that, the white precipitate was filtered out, and the filtrate was evaporated by rotary evaporation. The crude product was further purified by flash column chromatography on silica gel using hexane as the eluent to afford the product OPOSS-vinyl (7.30g, 5.91 mmol) as a clear viscous liquid. Yield 59%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 6.12 – 5.84 (m, 3H), 1.97 – 1.75 (m, 7H), 1.40 – 1.09 (m, 14H), 1.07 – 0.98 (m, 21H), 0.96 – 0.87 (m, 63H), 0.83 – 0.53 (m, 14H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 135.75, 130.03, 54.01, 31.14, 30.14, 25.64, 24.99, 23.64.

2. OPOSS-S-OH

OPOSS-vinyl (3.7 g, 3 mmol), 2-mercaptoethanol (254 mg, 3.3 mmol) and photoinitiator (Irgacure 2959) (7.3 mg, 0.033 mmol) were dissolved in 30 mL THF. After illuminated under 365 nm UV light for 15 min, THF was fully removed by rotary evaporation then dried in vacuo. The resulting mixture was dissolved in 100 mL hexane then washed with water (100 mL x 2), brine (100 mL) dried over Na$_2$SO$_4$, concentrated by rotary evaporation to afford the crude product. The crude product was further purified by flash column chromatography on silica gel using hexane and DCM.
(v/v = 5/1) as the eluent to afford the product OPOSS-S-OH (2.8 g, 2.1 mmol) as a clear viscous liquid. Yield 70%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 3.71 (dd, 2H), 2.74 (t, 2H), 2.68 – 2.60 (m, 2H), 2.14 (t, 1H), 1.83 (s, 7H), 1.24 (d, 14H), 1.07 – 0.96 (m, 21H), 0.96 – 0.82 (m, 63H), 0.81 – 0.49 (m, 14H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 59.95, 53.94, 35.07, 31.13, 30.13, 25.56, 24.98, 23.58, 13.78.

3. OPOSS$_{01}$

OPOSS-vinyl (1.23 g, 1.0 mmol), t-butylthiol (135 mg, 1.5 mmol) and photoinitiator (Irgacure 2959) (3.2 mg, 0.015 mmol) were dissolved in 10 mL THF. After illuminated under 365 nm UV light for 15 min, THF was fully removed by rotary evaporation then dried in vacuo. The crude product was further purified by flash column chromatography on silica gel using hexane as the eluent to afford the product OPOSS$_{01}$ (730 mg, 0.55 mmol) as a clear viscous liquid. Yield 55%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 2.71 – 2.55 (m, 2H), 1.94 – 1.75 (m, 7H), 1.33 (s, 9H), 1.37 – 1.10 (m, 9 + 14 H), 1.07 – 0.98 (m, 21H), 0.91 (s, 64H), 0.83 – 0.52 (m, 14H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 54.13, 42.21, 31.34, 31.17, 30.34, 25.83, 25.19, 23.67, 22.54, 13.63.

$^{29}$Si NMR (99 MHz, CDCl$_3$) δ -67.82, -68.20, -70.07.

4. N$_3$-COOH

To a solution of 4-aminobenzoic acid (0.75 g, 5.5 mmol) in water (20 mL) in an ice-water bath, 2mL of concentrate HCl solution was added dropwise. Then a solution of NaNO$_2$ (415 mg, 6.0 mmol) in water (5 mL) was added dropwise. Pale-yellow precipitate was formed during the addition. After that, the reaction mixture was stirred at 0°C for another 30 min. Then, a solution of NaN$_3$ (390 mg, 6.0 mmol) in water (5 mL) was added dropwise to the previous solution while keep the temperature below 5 °C. The reaction mixture was stirred at room temperature for 14 h, filtered, washed with water and dried in vacuum. N$_3$-COOH was obtained in 85% yield (0.67g, 4.7 mmol) as a pale-yellow solid.

$^1$H NMR (300 MHz, DMSO-d$_6$) δ 12.98 (br, 1H), 7.96 (d, 2H), 7.21 (d, 2H).

$^{13}$C NMR (75 MHz, DMSO-d$_6$) δ 167.00, 144.39, 131.66, 127.73, 119.61.

5. N$_3$-OPOSS

To a 50mL round-bottomed flask equipped with a magnetic stirring bar were added OPOSS-S-OH (2.61g, 2.0mmol), N$_3$-COOH (280mg, 2.1mmol) and DPTS (58.6 mg, 0.2mmol), followed by the addition of 30 mL freshly dried THF to dissolved the reactant. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (350µL, 2.1mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 14 h at room temperature. Then the THF was fully removed by rotary evaporation and vacuo dry to afford the crude product. The
crude product was further purified by flash column chromatography on silica gel using hexane and DCM mixture (v/v = 4:1) as the eluent to afford the product (2.48g, 1.7mmoml) as a clear viscous liquid. Yield 85%.

1H NMR (500 MHz, CDCl3) δ 8.05 (d, 2H), 7.07 (d, 2H), 4.45 (t, 2H), 2.89 (t, 2H), 2.73 (t, 2H), 1.96 – 1.75 (m, 7H), 1.41 – 1.09 (m, 14H), 1.08 – 0.98 (m, 21H), 0.97 – 0.84 (m, 63H), 0.83 – 0.53 (m, 14 + 2H).

13C NMR (126 MHz, CDCl3) δ 165.33, 144.83, 131.46, 126.66, 118.80, 63.82, 53.94, 31.14, 30.34, 30.16, 26.69, 25.58, 24.99, 23.60, 13.79.

29Si NMR (99 MHz, CDCl3) δ -67.75, -68.17, -70.44.

MALDI-TOF MS [C67H131N3O14SSi8 + Ag]⁺: Calcd. 1565.6, found 1564.7.

6. N3-2COOH
To a solution of 5-aminoisophthalic acid (1.00 g, 5.5 mmol) in water (10 mL) in an ice-water bath, 2mL concentrate HCl solution was added dropwise. Then a solution of NaNO2 (415 mg, 6.0 mmol) in water (5 mL) was added dropwise. Pale-yellow precipitate was formed during the addition. After that, the reaction mixture was stirred at 0°C for another 30 min. Then, a solution of NaN3 (390 mg, 6.0 mmol) in water (5 mL) was added dropwise to the previous solution while keep the temperature below 5 °C. The reaction mixture was stirred at room temperature for 14 h, filtered, washed with water and dried in vacuum. The compound N3-2COOH was obtained in 85% yield (0.97g, 4.7 mmol) as a pale-yellow solid.

7. N3-2OPOSS
To a 50mL round-bottomed flask equipped with a magnetic stirring bar were added OPOSS-S-OH (2.61g, 2.0mmol), N3-2COOH (227mg, 1.1mmol) and DPTS (58.6 mg, 0.2mmol), followed by the addition of 30 mL freshly dried THF to dissolved the reactant. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (350µL, 2.1mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 14 h at room temperature. Then the THF was fully removed by rotary evaporation and vacuo dry to afford the crude product. The crude product was further purified by flash column chromatography on silica gel using hexane and DCM mixture (v/v = 4:1) as the eluent to afford the product (2.23g, 0.8mmoml) as a clear viscous liquid. Yield 80%.

1H NMR (500 MHz, CDCl3) δ 8.46 (s, 1H), 7.88 (d, 2H), 4.48 (t, 4H), 2.90 (t, 4H), 2.78 – 2.67 (m, 4H), 1.85 (s, 14H), 1.48 – 1.10 (m, 28H), 1.03 (d, 42H), 0.92 (d, 126H), 0.74 (m, 28 + 4H).

13C NMR (126 MHz, CDCl3) δ 164.44, 141.28, 132.34, 126.99, 124.08, 64.12, 53.91, 31.13, 30.17, 29.47, 26.58, 25.62, 24.99, 23.60, 13.74.

29Si NMR (99 MHz, CDCl3) δ -67.75, -68.18, -70.47.

MALDI-TOF MS [C67H131N3O14SSi8 + Ag]⁺: Calcd. 2904.9, found 2903.5.

8. CH3OOC-yne
A mixture of methyl hydroxybenzoate (3.04 g, 20 mmol), propargyl bromide (80% wt in toluene, 6.8 mL, 22 mmol), K2CO3 (5.50 g, 40 mmol), in acetone (100 mL) was
heated to reflux for 15 h. The solid was removed by filtration and the solvents were removed by rotary evaporation. Water (100 mL) was added and the mixture was extracted with 100mL CH2Cl2. The organic phase was dried over anhydrous Na2SO4, and the solvent was removed in vacuum to give the product as a white powder (3.61g, 21mmol) in 95% yield.

1H NMR (500 MHz, CDCl3) δ 8.01 (d, 2H), 7.00 (d, 2H), 4.74 (d, 2H), 3.89 (s, 3H), 2.54 (t, 1H).

13C NMR (125 MHz, CDCl3) δ 166.40, 151.48, 141.40, 125.95, 110.20, 78.87, 78.13, 76.30, 75.69, 60.50, 57.30, 52.48.

9. HOOC-yn

Lithium hydroxide (LiOH, 360 mg, 15 mmol) was added to a solution of CH3OOC-yn (1.90 g, 10 mmol) in Methanol (50 mL). The mixture was stirred at room temperature for 14 h. Then, the solution was condensed by rotary evaporation. HCl (2.0 M) was added dropwise to the mixture to adjust the pH ≈ 2, The mixture was filtered, washed with water and dried in vacuo to afford the product as a white powder (1.67g, 9.5mmol) in 95% yield.

1H NMR (300 MHz, DMSO-d6) δ 7.88 (d, 2H), 7.05 (d, 2H), 4.87 (d, 2H), 3.60 (t, 1H).

13C NMR (75 MHz, DMSO-d6) δ 166.87, 160.72, 131.24, 123.69, 114.65, 78.74, 78.59, 55.65.

10. CH3OOC-3yne

A mixture of methyl 3,4,5-trihydroxybenzoate (3.68 g, 20 mmol), propargyl bromide (80% wt in toluene, 7.2 mL, 66 mmol), K2CO3 (11.0 g, 80 mmol), in acetone (100 mL) was heated to reflux for 14 h. The solid was removed by filtration and the acetone was removed by rotary evaporation. Water (100 mL) was added and the mixture was extracted with 100mL CH2Cl2. The organic phase was dried over anhydrous Na2SO4 and the solvent was removed in vacuum to give the product as a white powder (5.66 g, 19 mmol) in 95% yield.

1H NMR (500 MHz, CDCl3) δ 7.48 (s, 2H), 4.83 (d, 2H), 4.81 (d, 4H), 3.92 (s, 3H), 2.53 (t, 2H), 2.46 (s, 1H).

13C NMR (125 MHz, CDCl3) δ 166.23, 151.31, 141.22, 125.77, 110.03, 78.70, 77.96, 76.13, 75.52, 60.33, 57.13, 53.38, 52.31.

11. HOOC-3yne

LiOH (960 mg, 40 mmol) was added to a solution of Compound CH3OOC-3yne (2.98 g, 10 mmol) in Methanol (100 mL). The mixture was stirred at room temperature for 14 h, The solvent was removed by rotary evaporation and HCl (2.0 M) was added to the mixture to adjust the pH ≈ 2. The mixture was filtered, washed with water and dried in vacuo to afford the desired product as a white powder (2.69 g, 9.5 mmol) in yield 95%.

1H NMR (300 MHz, DMSO-d6) δ 7.36 (s, 2H), 4.87 (d, 4H), 4.70 (d, 2H), 3.59 (t, 3H).
13C NMR (75 MHz, DMSO-d6) δ 166.61, 150.93, 139.79, 126.30, 109.00, 79.09, 78.87, 78.73, 78.27, 59.51, 56.54.

12. HPOSS

VPOSS (1.29g, 2mmol), 2-mercaptoethanol (1.56g, 20mmol), and photoinitiator (Irgacure 2959) (43mg, 0.2mmol) were dissolved in 10 mL of THF. After irradiation for 10 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with THF/CH2Cl2 (v/v=1/1) as the eluent afford the crude product, the crude product was dissolved in 1mL of THF then added dropwise into 10 mL of EA to afford white precipitate. The precipitate was further filtered and dry in vacuum to afford the pure HPOSS (hydroxyl functionalized POSS) as white powder (1.02g, 0.8mmol).

1H NMR (500 MHz, DMSO-d6) δ 4.72 (t, J = 5.5 Hz, 1H), 3.52 (dd, J = 12.5, 6.8 Hz, 2H), 2.71–2.53 (m, 4H), 0.99 (t, 2H).

13C NMR (126 MHz, DMSO-d6) δ 61.70, 40.45, 34.58, 26.27, 13.54.

29Si NMR (99 MHz, DMSO-d6) δ -68.45.

13. POSS-8yne

To a 50mL round-bottomed flask equipped with a magnetic stirring bar were added HPOSS (127mg, 0.1mmol), HOOC-yne (530mg, 3mmol) and DPTS (87.9 mg, 0.3mmol), followed by the addition of 20 mL freshly dried CH2Cl2 to dissolve the reactant. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (464 µL, 3.0 mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 48 h at room temperature. Then the solution was concentrated and directly transferred onto a silica gel column a mixture of CH2Cl2 and ethyl acetate (v/v = 20/1) was used to flash out the crude product, the crude product further was purified by THF size exclusion chromatography afford clear viscous liquid (152mg, 0.06mmol) in yield 60%.

1H NMR (500 MHz, CDCl3) δ 7.96 (d, 16H), 6.95 (d, 16H), 4.71 (d, 16H), 4.40 (t, 16H), 2.86 (t, 16H), 2.72 (t, 16H), 2.54 (t, 8H), 1.09 (t, 16H).

13C NMR (126 MHz, CDCl3) δ 165.82, 161.23, 131.61, 123.27, 114.51, 77.83, 76.11, 63.47, 55.83, 30.42, 26.28, 13.06.

29Si NMR (99 MHz, CDCl3) δ -68.88.

MALDI-TOF MS [C112H120O36S8Si8 +Na]+ Calcd. 3543.34, found 2543.317.

14. OPOSS16

To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added POSS-8yne (76mg, 0.03mmol), N3-2OPOSS (805mg, 0.29mmol), CuBr (5mg, 0.03mmol), and 30 mL toluene. The solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (10mg, 0.06mmol) under the protection of nitrogen gas. The mixture was degassed by one more freeze-pump-thaw cycle and then stirred at room temperature for 24 h. Then the solution was further condensed by rotary evaporation and directly transferred onto a silica gel column. CH2Cl2 was used to remove any unreacted 2OPOSS-N3. Then, a
mixture of CH$_2$Cl$_2$ and ethyl acetate (v/v = 5/1) was used to flash the crude product out of the column. The product was purified by THF size exclusion chromatography afford clear viscous liquid (622mg, 0.025mmol) in yield 83%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.73 (s, 1×8 H), 8.63 (s, 2×8 H), 8.25 (s, 1×8 H), 8.02 (d, J = 8.8 Hz, 2×8H), 7.04 (d, 2×8 H), 5.33 (s, 2×8 H), 4.51 (t, 4×8 H), 4.45 (t, 2×8 H), 2.91 (t, 6×8 H), 2.83 – 2.74 (m, 2×8 H), 2.75 – 2.68 (m, 4×8 H), 1.83 (s, 14×8H), 1.39 – 1.07 (m, 28×8 H), 1.09 – 0.97 (m, 42×8 H), 0.95 – 0.84 (m, 126×8 H), 0.82 – 0.51 (m, (32 + 2)×8 H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.84, 164.09, 161.93, 144.80, 137.35, 132.56, 131.82, 130.55, 125.27, 123.26, 121.06, 114.30, 64.45, 63.40, 61.96, 53.92, 31.13, 30.13, 26.62, 25.62, 23.58, 13.72.

$^{29}$Si NMR (99 MHz, CDCl$_3$) δ -67.76, -68.19, -68.89, -70.55.

15. POSS-24yne

To a 50mL round-bottomed flask equipped with a magnetic stirring bar were added HPOSS (127mg, 0.1mmol), HOOC-3yne (852mg, 3mmol) and DPTS (87.9 mg, 0.3mmol), followed by the addition of 20 mL freshly dried CH$_2$Cl$_2$ to dissolved the reactant. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (464 µL, 3.0 mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 48 h at room temperature. Then the solution was concentrated and directly transferred onto a silica gel column a mixture of CH$_2$Cl$_2$ and ethyl acetate (v/v = 20/1) was used to flash out the crude product, the crude product further was purified by THF size exclusion chromatography afford clear viscous liquid (203mg, 0.06mmol) in yield 60%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 (s, 16H), 4.82 (d, 16H), 4.79 (d, 32H), 4.43 (t, 16H), 2.89 (t, 16H), 2.75 (t, 16H), 2.56 (t, 16H), 2.47 (t, 8H), 1.12 (t, 16H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.46, 151.31, 141.44, 125.48, 110.20, 78.68, 78.04, 76.29, 75.64, 63.75, 60.33, 57.21, 30.29, 26.22, 13.09.

$^{29}$Si NMR (99 MHz, CDCl$_3$) δ -68.87.

MALDI-TOF MS [C$_{160}$H$_{152}$O$_{52}$S$_{8}$Si$_{8}$ +Na]$^+$: Calcd. 3407.51 found 3406.776.

16. OPOSS$_{24}$

To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added POSS-24yne (26mg ,0.01mmol), N$_3$-OPOSS (1.12g, 0.4mmol), CuBr (6mg, 0.04mmol), and 30 mL toluene. The solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (15mg, 0.08mmol) under the protection of nitrogen gas. The mixture was degassed by one more freeze-pump-thaw cycle and then stirred at room temperature for 24 h. Then the solution was further condensed by rotary evaporation and directly transferred onto a silica gel column. CH$_2$Cl$_2$ was used to remove any unreacted OPOSS-N$_3$. Then, a mixture of CH$_2$Cl$_2$ and ethyl acetate (v/v = 5/1) was used to flash the crude product out of the column. The product was purified by THF size exclusion chromatography afford clear viscous liquid (300mg, 0.008mmol) in yield 80%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.53 (s, 2×8 H), 8.37 (s, 1×8 H), 8.14 (d, 4×8 H), 8.10
(d, 2×8 H), 7.90 (d, 4×8 H), 7.80 (d, 2×8 H), 7.42 (s, 2×8 H), 5.30 (s, 4×8 H), 5.27 (s, 2×8 H), 4.57 – 4.49 (m, 2×8 H), 4.46 (t, 6×8 H), 3.05 – 2.95 (m, 2×8 H), 2.94 – 2.82 (m, 8×8 H), 2.79 – 2.65 (m, 6×8 H), 1.83 (s, 21×8 H), 1.42 – 1.07 (m, 42×8 H), 1.00 (d, 63×8 H), 0.90 (s, 189×8 H), 0.81 – 0.50 (m, (48+2)×8 H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.37, 164.90, 164.86, 151.99, 145.11, 144.51, 141.60, 139.91, 139.85, 131.33, 131.30, 130.16, 130.10, 125.89, 121.99, 121.53, 119.75, 119.66, 109.13, 66.09, 63.99, 63.15, 53.91, 30.14, 26.65, 24.97, 23.58, 13.76.

$^{29}$Si NMR (99 MHz, CDCl$_3$) δ -67.77, -68.20, -68.82, -70.51.
Figure S1. Synthesis routes towards (a) OPOSS-S-OH and OPOSS$_01$ (b) N$_3$-OPOSS (c) N$_3$-2OPOSS
Figure S2. Synthesis routes towards (a) HOOC-yne (b) HOOC-3yne
Figure S3. Synthesis routes towards OPOSS$_{16}$ and OPOSS$_{24}$
Figure S4. $^1$H NMR spectrum of HPOSS.
Figure S5. $^{13}$C NMR spectrum of HPOSS
Figure S6. $^{29}$Si NMR spectrum of HPOSS.
Figure S7. $^1$H NMR spectrum of OPOSS-vinyl
Figure S8. OPOSS-vinyl $^{13}$C NMR (126 MHz, CDCl$_3$)
Figure S9. OPOSS-S-OH $^1$H NMR (500 MHz, CDCl$_3$)
Figure S10. $^{13}$C NMR spectrum of OPOSS-S-OH.
Figure S11. $^1$H NMR spectrum of OPOSS$_{01}$. 
Figure S12. $^{13}$C NMR spectrum of OPOSS$_{01}$.
Figure S13. $^{29}$Si NMR spectrum of OPOSS$_{01}$. 
Figure S14. $^1$H NMR spectrum of POSS-8yne.
Figure S15. $^{13}$C NMR spectrum of POSS-8yne.
Figure S16. $^{29}$Si NMR spectrum of POSS-8yne.
Figure S17. POSS-8yne MALDI-TOF MS result

\[ [C_{112}H_{120}O_{36}S_8Si_8 + Na]^+ \text{ Calc.} = 2543.34 \]

Found \[ [C_{112}H_{120}O_{36}S_8Si_8 + Na]^+ = 2543.317 \]

\[ [C_{112}H_{120}O_{36}S_8Si_8 + Na + O]^+ = 2559.275 \]
Figure S18. $^1$H NMR spectrum of POSS-24yne.
Figure S19. $^{13}$C NMR spectrum of POSS-24yne.
Figure S20. $^{29}$Si NMR spectrum of POSS-24yne.
Figure S21. POSS-24yne MALDI-TOF MS result

\[ \text{[C}_{160}\text{H}_{152}\text{O}_{52}\text{S}_{8}\text{Si}_{8} + \text{Na}]^+ \text{ Calc.} = 3407.51} \]

\[ \text{Found [C}_{160}\text{H}_{152}\text{O}_{52}\text{S}_{8}\text{Si}_{8} + \text{Na}]^+ = 3406.776} \]
Figure S22. $^1$H NMR spectrum of OPOSS$_{16}$. 
Figure S23. $^{13}$C NMR spectrum of OPOSS$_{16}$.
Figure S24. $^{29}$Si NMR spectrum of OPOSS\textsubscript{16}.
Chemical shifts at -67.77, -68.19, and -70.55 ppm can be assigned to Si atoms of OPOSS cages at ortho, meta and para, joint positions respectively, while the chemical shift at -68.89 ppm can be assigned to Si atoms on the core POSS cage.
Figure S25. OPOSS$_{16}$ MALDI-TOF MS result

$[\text{C}_{1136}\text{H}_{2176}\text{N}_{24}\text{O}_{260}\text{S}_{24}\text{Si}_{136} + \text{Ag}]^+$

Theoretical average m/z is 25030.7

Observed average m/z Found 25030.7

The major fragmentation loses two OPOSS and happens likely at phenoxy region.
Figure S26. OPOSS$_{16}$ GPC traces

Mn = 1.70 × 10$^4$
Mw = 1.83 × 10$^4$
Mz = 1.94 × 10$^4$
PDI = 1.06, would be intrinsic from the instrument.
Figure S27. $^1$H NMR spectrum of OPOSS$_{24}$
Figure S28. $^{13}$C NMR spectrum of OPOSS$_{24}$. 
Figure S29. $^{29}$Si NMR spectrum of OPOSS$_{24}$. 
Figure S30. OPOSS$_{24}$ MALDI-TOF MS result

$[C_{1768}H_{3296}N_{72}O_{388}S_{32}Si_{200} + Ag]^+$

Theoretical average m/z is 38524.8

Observed average m/z Found 38525.3

Because of their high molecular weights, fractures are inevitable during the ionization process of MALDI-TOF-MS. The major fragmentation loses one OPOSS (two OPOSS for OPOSS$_{16}$) and happens most likely at phenoxy region.
Figure S31. OPOSS$_{24}$ GPC traces

$M_n = 2.00 \times 10^4$

$M_w = 2.19 \times 10^4$

$M_z = 2.33 \times 10^4$

$PDI = 1.07$
Figure S32. SAXS patterns of OPOSS\(_{01}\), OPOSS\(_{16}\) and OPOSS\(_{24}\) in bulk state. The broad correlation peak at 1.3 nm corresponds to the characteristic diameter of individual OPOSS. OPOSS\(_{16}\) and OPOSS\(_{24}\) in bulk state only possess short-range orders. The broad correlation peaks at low q are very close for OPOSS\(_{16}\) and OPOSS\(_{24}\), not reflecting the diameter of giant molecules.

From a dendrimer point of view, OPOSS\(_{16}\) and OPOSS\(_{24}\) are of the same first generation. The conformation of OPOSS\(_{16}\) in the bulk is not an ideal sphere-like. The characteristic scattering may be an average of many different detecting angles, and resulted in this observation. In other words, the corresponding \(d_s\) of 4.3 and 4.4 nm originates from 2 times the linker length.
**Figure S33.** Raw data and smoothed SAXS curves of two samples in solutions and of solvent as background.
Figure S34. SAOS of OPOSS$_{16}$ at different temperatures were used to construct the master curves.
Figure S35. SAOS of OPOSS$_{24}$ at different temperatures were used to construct the master curves.