Supporting Information

Toward Controlled Hierarchical Heterogeneities in Giant Molecules with Precisely Arranged Nano-Building Blocks

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Materials and Characterizations

Styrene (Acros Organic, 99.5%) was purified by filtering through a silica gel column to remove the inhibitor; octavinyl POSS and monovinylisobutyl POSS were purchased from Hybrid Plastics and used as received; other chemicals and solvents were used as received from Sigma-Aldrich, Acros Organic, or Fisher Scientific. VPOSS-diOH \(^1\), DIBO-VPOSS-CHO \(^2\), the linear “click adaptor" \(^3\) and 4-(azidomethyl)benzoic acid \(^4\) were synthesized according to previous literatures.

\(^1\)H and \(^13\)C NMR experiments were measured on a Varian Mercury 500 NMR or 300 NMR spectrometer. \(^1\)H NMR spectra were referenced to the residual solvent peak in CDCl\(_3\) at \(\delta 7.27\) ppm, and \(^13\)C NMR spectra were referenced to the solvent peak of CDCl\(_3\) at \(\delta 77.00\) ppm, respectively.

Infrared spectra were measured on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by drop-casting sample films on a KBr disk from THF solution (~10 mg/mL).

UV-Vis absorption spectra were measured using Ocean Optics, Inc. Chem2000 UV-Vis spectrophotometer. The concentration is about \(10^{-4}\) mol/L in CHCl\(_3\).

Gel permeation chromatography (GPC) were measured at 35 °C on a Waters 150-C Plus instrument with three HR-Styragel columns [100 Å, mixed bed (50/500/10^3/10^4 Å), mixed bed (10^3, 10^4, 10^6 Å)] and a triple detector system (a refractometer, a 670 nm laser light scattering detector and a differential viscometer). The flow rate of THF was 1.0 mL/min.

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 polymer molecules.

Samples for Small angle X-ray scattering (SAXS) were prepared by thermal annealing under N\(_2\) atmosphere at 120 °C to 150 °C for several hours. The experiments were recorded on a micromax003+ machine. The wavelength of the X-ray is 0.154 nm. The working voltage is 55 kV and current is 0.6 mA.

A Reichert Ultracut S (Leica) microtome was used to make the thin slices of bulk samples for TEM experiments. Bright field TEM images were collected on a JEOL-1230 TEM with an accelerating voltage of 120 kV.

Calculation of volume fractions in the giant molecules:

\[
v_f^{POSS} = \frac{n(M_{POSS} + M_{ linker})/\rho_{POSS}}{M_{PS}/\rho_{PS} + n(M_{POSS} + M_{ linker})/\rho_{POSS}}
\]

where \(M_{POSS} = 1.5\) kg/mol, \(M_{PS} = 14\) kg/mol, 8.5 kg/mol or 2.8 kg/mol, \(\rho_{POSS} = 1.43\) g/cm\(^3\), \(n\) is the number of POSS heads. The same formula can be utilized to calculate the \(v_f^{POSS}\) in PS_m-(HPOSS)_n by applying \(M_{HPOSS} = 1.3\) kg/mol and the measured density of \(\rho_{HPOSS} = 1.28\) g/cm\(^3\).

Calculation of number of molecules in one aggregated DPOSS sphere in BCC

\[
\mu = \frac{V_{cell}}{2(V_{PS0} + V_{POSS0})} = \frac{(\sqrt{2}d_1)^3N_A}{2[M_{PS}/\rho_{PS} + n(M_{POSS} + M_{ linker})/\rho_{POSS}]}\]
For PS\(_{135}\)-DPOSS, the distance between two neighboring DPOSS spheres is 12.3 nm; while the DPOSS core diameter is (6.4 ± 0.4) nm and the PS tail matrix between two spheres is (5.9 ± 0.4) nm.

Calculation of number of molecules of one DPOSS thickness (h=1.4 nm) in HEX

\[
\mu = \frac{V_{\text{cell}}}{(V_{PS0} + V_{POSS0})} = \frac{2d_1^2 hN_A}{\sqrt{3]\left[ M_{PS}/\rho_{PS} + n(M_{POSS} + M_{\text{linker}})/\rho_{POSS}\right]}
\]

Taking PS\(_{135}\)-(DPOSS)\(_2\) as an instance, the cylindrical core sizes are (7.6 ± 0.4) nm and the PS matrices are (10.2 ± 0.4) nm along the distance between two centers of the neighboring cylinders. We thus can estimate that there are roughly 14 DPOSS cages closely packed in a unit volume with one DPOSS thickness (1.4 nm) along the long cylinder axis.

Calculation of cross-section area of each PS chain in the lamellae

\[
A_{PS} = \frac{V_{PS}}{d_{PS}/2} = \frac{2M_{PS}}{\rho_{PS}N_A d_{PS}}
\]

Cross-section area of DPOSS (diameter = 1.4 nm) and HPOSS (diameter = 1.2 nm)

\[
A_{\text{DPOSS}} = \pi r_{\text{DPOSS}}^2 = 1.5 \text{ nm}^2
\]

\[
A_{\text{HPOSS}} = \pi r_{\text{HPOSS}}^2 = 1.1 \text{ nm}^2
\]

For example, PS\(_{83}\)-(DPOSS)\(_3\) with \(\nu_f^{\text{POSS}} = 0.36\), for example, the overall long period is 14.3 nm in which the DPOSS layer thickness is (5.5 ± 0.4) nm and the PS tail layer is (8.8 ± 0.4) nm, respectively. The cross-section area of PS tails (m = 83) is \(~2.7 \text{ nm}^2\), approximately twice that of DPOSS cages (~1.5 nm\(^2\)). A plausible packing model is thus proposed that the linearly configured DPOSS cages are along the layer normal, yet the head-to-head alignment is interdigitated to pack the molecules into one and a half layers. Other LAMs of PS\(_{83}\)-(DPOSS)\(_n\) and PS\(_{135}\)-(DPOSS)\(_n\) (n = 3, 4, and 5) are also packed in this lamellar model. Specifically, the observed DPOSS layer thicknesses for all of these giant molecules are proportional to the number of DPOSS cages in each of these giant molecules along the lamellar normal.

There is another kind of LAM packing model in the case of, e.g., PS\(_{27}\)-DPOSS with \(\nu_f^{\text{POSS}} = 0.37\). Its overall long period is 8.08 nm, while the DPOSS lamellar thickness is (3.0 ± 0.3) nm and the PS layer thickness is (5.08 ± 0.3) nm. Comparing the cross-section areas of DPOSS (~1.5 nm\(^2\)) and PS\(_{27}\) (~1.7 nm\(^2\)), there is only a minor difference between these two cross-section areas, which suggests that the PS tails are perhaps slightly stretched along the layer normal. Therefore, a simple head-to-head arrangement of double layered DPOSS and PS domains is evoked.

Calculation of number of molecules in inversed HEX:

\[
\mu = \frac{V_{PS}}{(V_{PS0})} = \frac{\pi (d_{PS}/2)^2 hN_A}{M_{PS}/\rho_{PS}}
\]

For, PS\(_{27}\)-(DPOSS)\(_3\), PS\(_{27}\)-(DPOSS)\(_4\)and PS\(_{27}\)-(DPOSS)\(_5\), the PS tails are now located within the columnar cores and the DPOSS cages are in the matrix. Since their PS tails in these three samples are the same, the sizes of the cylindrical cores for these
three samples are almost identical ((7.0 ± 0.3) nm). We can thus calculate that the number of PS tails in a unit volume with one DPOSS thickness (1.4 nm) along the long cylinder axis to be ∼12. The sizes of DPOSS matrices are (4.3 ± 0.2) nm, (5.1 ± 0.2) nm and (6.9 ± 0.4) nm, respectively, along the distance between two centers of the neighboring cylinders. Comparing these sizes with those in the interdigitated packing model in the LAM structure, we speculate that the DPOSS cages are also packed in a relatively stretched and partly interdigitated way.
Scheme S1. Syntheses of (a) linear PS-(HPOSS)$_n$ and PS-(DPOSS)$_n$ and (b) PS-(XPOSS)$_n$.
Scheme S2. Syntheses of dendritic PS-Gx-(HPOSS)$_n$
**Synthetic Procedures**

**HO-2N₃ (1).** To a solution of 4-(azidomethyl)benzoic acid (708 mg, 4.00 mmol), 1,1,1-tris(hydroxymethyl)ethane (240 mg, 2.00 mmol), 4-dimethylaminopyridine (DMAP) (48 mg, 0.40 mmol) in anhydrous CH₂Cl₂, N,N'-diisopropylcarbodiimide (DIPC) (504 mg, 4.00 mmol) was added dropwise at 0 °C in ice-water bath. The solution was then stirred at ambient temperature for 12 h. The precipitate was filtered and the filtrate was washed with water and dried by anhydrous Na₂SO₄. After solvent removal, the residue was purified by a silica gel column (CH₂Cl₂/ethyl acetate = 10/1) to afford the product (481 mg, 1.10 mmol) in 55% yield. ¹H NMR (CDCl₃, 500MHz, ppm, δ) 8.01 (d, 2H, Ar-H), 7.34 (d, 2H, Ar-H), 4.40-4.34 (m, 8H, lCH₂lN₃lCOOCH₂l), 3.62 (d, 2H, lCH₂lOH), 2.95 (s, 1H, lOH), 1.14 (s, 3H, lCH₃). ¹³C NMR (CDCl₃, 125MHz, ppm, δ) 166.04, 140.63, 129.94, 129.46, 127.80, 66.68, 64.42, 53.97, 40.58, 16.82.

**BocNH-2N₃ (2).** HO-2N₃ (355 mg, 0.81 mmol), (Boc-aminoxy)acetic acid (155 mg, 0.81 mmol), DMAP (9.9 mg, 0.08 mmol) were dissolved in anhydrous CH₂Cl₂. DIPC (204 mg, 1.62 mmol) were added dropwise under 0 °C in ice-water bath. After the addition, the mixture was stirred at ambient temperature for 12 h. The precipitate was filtered and the filtrate was washed with water and dried by anhydrous Na₂SO₄. The solution was concentrated a rotary evaporator, and the residue was suffered a silica gel column (CH₂Cl₂/ethyl acetate = 10/1) to afford the product (300 mg, 0.49 mmol) in 60% yield. ¹H NMR (CDCl₃, 500MHz, ppm, δ) 8.02 (d, 2H, Ar-H), 7.90 (s, 1H, lCONHl), 7.38 (d, 2H, Ar-H), 4.44 (s, 2H, lOCH₂COOl), 4.41 (s, 4H, ArCOOCH₂l), 4.39 (s, 4H, lCH₂lN₃l), 4.30 (s, 2H, lCOOCH₂l), 1.46 (s, 9H, lC(CH₃)₃), 1.20 (s, 3H, lCH₃). ¹³C NMR (CDCl₃, 125MHz, ppm, δ) 169.28, 165.60, 156.21, 140.85, 130.06, 129.40, 127.96, 82.02, 72.34, 66.38, 66.30, 54.11, 41.96, 39.06, 28.05, 23.38, 17.32.

**The dendritic “click adaptor” (3).** BocNH-2N₃ (300 mg, 0.49 mmol) was stirred in a hydrochloric acid solution (3 mL, 1 M in dioxane) for 5 h. After the reaction, the access hydrochloric acid solution was removed by vacuum to afford the product (260 mg, 0.46 mmol) in 99% yield. ¹H NMR (CDCl₃, 500MHz, ppm, δ) 8.03 (m, 2H, Ar-H), 7.41 (d, 2H, Ar-H), 4.40-4.33 (m, 12H, -OCH₂COO- + -CH₂-N₃ + -COOCH₂-), 3.60 (s, 2H, -NH₂), 1.22 (s, 3H, -CH₃). ¹³C NMR (CDCl₃, 125MHz, ppm, δ) 168.51, 165.71, 140.84, 130.09, 129.42, 127.99, 125.44, 67.54, 66.48, 54.15, 38.99, 30.26, 23.26, 17.22.

**BPOSS-diOH (4a).** Monovinylisobutyl POSS (843 mg, 1.00 mmol), 2-mercaptopoethanol (216 mg, 2.00 mmol) and photoinitiator 2-Hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) (11.0 mg, 0.05 mmol) were dissolved in minimum THF. After illuminated under 365 nm UV light for 15 min, the product was obtained by precipitation into methanol/water (1:1) as a white powder (850 mg, 0.90 mmol) in 90% yield. ¹H NMR (CDCl₃, 500MHz, ppm, δ) 3.79 (m, 2H, -CH₂OH), 3.58 (m, 1H, -SCH₂CH₂l), 3.18 (s, 2H, -OH),
2.78-2.60 (m, 4H, -CH₂SCH₂-), 1.90-1.85 (m, 7H, (CH₃)₂CH-), 0.99-0.96 (m, 44H, CH₃- + SiCH₂CH₂Si-), 0.63-0.61 (m, 14 H, -SiCH₂CH₂Si-). ¹³C NMR (CDCl₃, 125MHz, ppm, δ) 69.47, 65.42, 35.56, 26.53, 25.66, 25.64, 23.87, 23.82, 22.46, 22.40.

General procedure for synthesizing tBuAPOSS-diOH, FPOSS-diOH and CIPOSS-diOH.

VPOSS-diOH (1.0 eq), thiol ligands (12.0 eq) and photoinitiator Irgacure 2959 (0.2 eq) were dissolved in minimum THF. After illuminated under 365 nm UV light for 15 min, the solvent was removed and the residue was purified by chromatography on silica gel using CH₂Cl₂/ ethyl acetate = 2/1 as eluent.

tBuAPOSS-diOH (4b). White solid (Yield 90%). ¹H NMR (CDCl₃, 500MHz, ppm, δ) 3.79 (m, 1H, lSCH₂CHl), 3.70 (m, 1H, lCH₂OH), 3.54 (m, 1H, lCH₂OH), 3.10 (s, 14H, lSCH₂COOl), 2.73l2.57 (m, 18H, lCH₂SCH₂l + lCH₂SCH₂COOl), 1.48l1.34 (m, 63H, CH₃l), 1.03l0.99 (m, 16H, lSiCH₂l).

FPOSS-diOH (4c). White solid (Yield 70%). ¹H NMR (CDCl₃, 500MHz, ppm, δ) 3.78 (m, 1H, lSCH₂CHl), 3.72 (m, 1H, lCH₂OH), 3.54 (m, 1H, lCH₂OH), 3.11l3.05 (m, 14H, lSCH₂CF₃), 2.77l2.57 (m, 18H, lCH₂SCH₂l + lCH₂SCH₂CF₃), 1.48l1.34 (m, 63H, CH₃l), 1.03l0.99 (m, 16H, lSiCH₂l). ¹³C NMR (CDCl₃, 125MHz, ppm, δ) 169.62, 169.43, 169.41, 81.40, 81.25, 81.23, 70.36, 653.26, 35.27, 34.51, 34.45, 34.52, 34.52, 27.90, 26.41, 26.34, 26.31, 12.84, 12.32.

ClPOSS-diOH (4d). Colorless liquid (Yield 80%). ¹H NMR (CDCl₃, 500MHz, ppm, δ) 3.77 (m, 1H, -SCH₂CH-), 3.72 (m, 1H, -CH₂OH), 3.54 (m, 1H, -CH₂OH), 3.11-3.05 (m, 14H, -SCH₂CF₃), 2.73-2.59 (m, 32H, -CH₂SCH₂l), 2.03-1.99 (m, 14H, ClCH₂CH₂l), 1.02-0.99 (m, 16H, -SiCH₂l). ¹³C NMR (CDCl₃, 125MHz, ppm, δ) 70.05, 69.88, 65.22, 43.57, 43.42, 43.24, 35.39, 32.08, 31.94, 28.82, 28.62, 28.41, 26.08, 25.88, 25.56, 12.86, 12.78, 12.68.

General procedure for synthesizing HO-XPOSS-CHO.

To a solution of XPOSS-diOH (1.0 eq), 4-formylbenzoic acid (0.9 eq) and DMAP (0.1 eq) in anhydrous CH₂Cl₂, DIPC (2.0 eq) was added dropwise at 0 °C. The solution was then stirred at ambient temperature for 12 h. The precipitate was filtered and the filtrate was washed with water and dried by anhydrous Na₂SO₄. After solvent removal, the residue was purified by a silica gel column (CH₂Cl₂ for HO-BPOSS-CHO, CH₂Cl₂/ ethyl acetate = 30/1 for HO-tBuAPOSS-CHO and HO-CIPOSS-CHO) to afford the product.

HO-BPOSS-CHO (5a). White solid (Yield 45%). ¹H NMR (CDCl₃, 500MHz, ppm, δ) 10.10 (s, 1H, -CHO), 8.21 (d, 2H, Ar-H), 7.95 (d, 2H, Ar-H), 4.49 (m, 1H, -CH₂OCO-), 4.41 (m, 1H, -CH₂OCO-), 4.10 (m, 1H, -SCH₂CH-), 2.83-2.66 (m, 4H, -CH₂OCH₂-).
-CH$_2$SCH$_2$-), 1.89-1.83 (m, 7H, (CH$_3$)$_2$CH-), 1.02-0.92 (m, 44H, CH$_3$- + \text{-SiCH$_2$CH$_2$S}-), 0.62-0.60 (m, 14H, -SiCH$_2$CH-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.42, 165.48, 139.34, 134.76, 130.30, 129.53, 129.49, 67.98, 67.76, 60.34, 35.91, 26.70, 25.66, 25.64, 23.67, 22.46, 22.40, 20.80, 14.17, 13.55.

**HO-tBuAPOSS-CHO (5b).** Colorless viscous liquid (Yield 50%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.08 (s, 1H, lCHO), 8.20 (d, 2H, Ar-H), 7.93 (d, 2H, Ar-H), 4.48 (m, 1H, lCH$_2$OOC-), 4.37 (m, 1H, lCH$_2$OOC-), 4.15 (m, 1H, -SCH$_2$CH-), 3.21 (q, 14H, lSCH$_2$COOl), 2.81-2.71 (m, 18H, lCH$_2$SCH$_2$ + lCH$_2$SCH$_2$COOl), 1.45-1.40 (m, 63H, CH$_3$-), 1.03-1.00 (m, 16H, -SiCH$_2$-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.41, 169.61, 169.44, 165.34, 139.18, 134.79, 130.23, 129.39, 81.39, 81.26, 68.58, 68.01, 35.49, 34.62, 34.55, 27.92, 27.91, 26.54, 26.43, 26.36, 12.85, 12.34.

**HO-FPOSS-CHO (5c).** Colorless viscous liquid (Yield 45%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.10 (s, 1H, lCHO), 8.21 (d, 2H, Ar-H), 7.95 (d, 2H, Ar-H), 4.50 (m, 1H, lCH$_2$OOC-), 4.40 (m, 1H, lCH$_2$OOC-), 4.12 (m, 1H, -SCH$_2$CH-), 3.08 (q, 14H, lSCH$_2$CF$_3$), 2.86-2.67 (m, 18H, -CH$_2$SCH$_2$ + -CH$_2$SCH$_2$CF$_3$), 1.06-1.03 (m, 16H, -SiCH$_2$-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.47, 165.52, 139.35, 134.65, 130.27, 129.48, 129.23, 127.03, 124.83, 122.63, 68.29, 67.97, 35.90, 34.62, 34.36, 34.10, 33.83, 27.17, 26.51, 12.73, 12.20.

**HO-ClPOSS-CHO (5d).** Colorless viscous liquid (Yield 40%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.11 (s, 1H, lCHO), 8.22 (d, 2H, Ar-H), 7.97 (d, 2H, Ar-H), 4.51 (m, 1H, lCH$_2$OOC-), 4.40 (m, 1H, lCH$_2$OOC-), 4.12 (m, 1H, -SCH$_2$CH-), 3.66 (m, 14H, ClCH$_2$-), 2.86-2.61 (m, 32H, lCH$_2$SCH$_2$ + lOOCCH$_2$CH$_2$COOl), 2.07-2.00 (m, 14H, ClCH$_2$CH$_2$-), 1.09-1.05 (m, 16H, -SiCH$_2$-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.45, 165.50, 139.35, 134.68, 130.31, 129.52, 68.35, 68.03, 43.52, 32.10, 28.79, 28.78, 26.70, 26.06, 25.96, 13.00, 12.94.

**General procedure for synthesizing DIBO-XPOSS-CHO.**

To a solution of HOlXPOSSlCHO (1.0 eq), DIBOlCOOH (1.0 eq) and DMAP (0.1 eq) in anhydrous CH$_2$Cl$_2$, DIPC (2.0 eq) was added dropwise at 0°C. The solution was allowed to warm up to ambient temperature and stirred for 12 h. The precipitate was filtered and the filtrate was washed with water and dried by anhydrous Na$_2$SO$_4$. After solvent removal, the residue was purified by a silica gel column (CH$_2$Cl$_2$ for HOlBPOSSlCHO, CH$_2$Cl$_2$/ethyl acetate = 30/1 for HOlBuAPOSSlCHO and HOlClPOSSlCHO) to afford the product.

**DIBO-BPOSS-CHO (6a).** White solid (yield 75%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.06 (d, 1H, -CHO), 8.14-7.80 (m, 4H, Ar-H), 7.53 (m, 1H, Ar-H), 7.40-7.23 (m, 7H, Ar-H), 5.58 (m, 1H, Ar-CHOOC-), 5.38 (m, 1H, -SCH$_2$CH-), 4.68 (m, 1H, -CH$_2$OOC-), 4.45 (m, 1H, -CH$_2$OOC-), 3.16 (dd, 1H, -CH$_2$CHOCO-), 2.94-2.68 (m, 10H, -CH$_2$CHOCO- + -CH$_2$SCH$_2$ + -OOCCH$_2$CH$_2$COO-), 1.89-1.86 (m, 7H, (CH$_3$)$_2$CH-), 0.98-0.90 (m, 44H, CH$_3$- + -SiCH$_2$CH$_2$S-), 0.64-0.62 (m, 14H,
$^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.45, 171.46, 170.76, 165.06, 150.84, 150.75, 139.26, 134.41, 130.25, 129.91, 129.41, 128.07, 127.94, 127.23, 127.13, 127.08, 126.26, 125.97, 125.87, 123.94, 123.82, 123.70, 123.65, 121.33, 112.95, 109.80, 70.79, 64.95, 46.28, 32.07, 29.19, 29.15, 29.04, 27.05, 25.66, 25.64, 23.85, 23.81, 22.46, 22.39, 22.7, 13.47. MALDI-TOF: (M·Na)$^+$ calc. for C$_{68}$H$_{99}$O$_{19}$F$_7$Si$_8$Na 1407.40, Found 1407.57.

**DIBO-tBuAPOSE-CHO (6b).** Light yellow viscous liquid (yield 65%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.06 (d, 1H, -CHO), 8.11-7.77 (m, 4H, Ar-H), 7.51 (m, 1H, Ar-H), 7.36-7.22 (m, 7H, Ar-H), 5.55 (m, 1H, Ar-CHO CO-), 5.37 (m, 1H, -SCH$_2$CH$_2$CO-), 4.66 (d, 1H, -CH$_2$O CO-), 4.44 (m, 1H, -CH$_2$OCO-), 3.18-3.12 (m, 15H, -CH$_2$CH$_2$CO- + SCH$_2$CO-), 2.91-2.67 (m, 23H, -CH$_2$CH$_2$CO- + -CH$_2$SCH$_2$- + OOCCH$_2$CH$_2$COO- + -OCCCH$_2$CH$_2$COO), 1.51-1.40 (m, 63H), 1.06-1.03 (m, 16H, -SiCH$_2$-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.49, 171.08, 170.04, 169.47, 165.03, 150.79, 139.19, 134.37, 132.10, 130.25, 129.85, 129.37, 128.04, 127.90, 127.20, 127.05, 126.26, 125.83, 125.19, 124.18, 124.03, 123.79, 123.59, 121.23, 112.89, 109.78, 70.73, 64.94, 46.22, 34.60, 29.15, 29.05, 28.00, 26.64, 26.41, 23.33, 12.88, 12.39. MALDI-TOF: (M·Na)$^+$ calc. for C$_{89}$H$_{134}$O$_{133}$F$_{21}$Si$_8$Na 2233.46, Found 2233.46.

**DIBO-FPOSS-CHO (6c).** Light yellow viscous liquid (yield 80%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.06 (d, 1H, -CHO), 8.13-7.80 (m, 4H, Ar-H), 7.51 (m, 1H, Ar-H), 7.34-7.24 (m, 7H, Ar-H), 5.56 (m, 1H, Ar-CHO CO-), 5.36 (m, 1H, -SCH$_2$CH$_2$-), 4.67 (d, 1H, -CH$_2$OCO-), 4.43 (m, 1H, -CH$_2$OCO-), 3.15-3.05 (q, 15H, -CH$_2$CH$_2$CO- + -CH$_2$SCH$_2$- + OOCCH$_2$CH$_2$COO-), 2.93-2.67 (23H, -CH$_2$CHO CO- + -CH$_2$SCH$_2$- + OOCCH$_2$CH$_2$COO), 1.07-1.04 (m, 16H, -SiCH$_2$-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.74, 171.59, 170.79, 165.10, 150.77, 139.30, 134.34, 130.39, 130.23, 129.40, 129.22, 128.50, 127.76, 127.51, 127.04, 126.74, 126.57, 125.76, 125.40, 124.83, 124.21, 123.65, 123.49, 122.62, 121.30, 112.94, 109.79, 71.23, 70.08, 46.28, 34.35, 34.04, 33.72, 33.17, 28.13, 27.76, 27.75, 26.78, 13.30, 12.54, 12.20. (M·Na)$^+$ calc. for C$_{61}$H$_{92}$O$_{19}$F$_{8}$Si$_8$Na 2009.01, Found 2009.12.

**DIBO-ClPOSS-CHO (6d).** Light yellow viscous liquid (yield 65%). $^1$H NMR (CDCl$_3$, 500MHz, ppm, δ) 10.06 (d, 1H, -CHO), 8.13-7.81 (m, 4H, Ar-H), 7.51 (m, 1H, Ar-H), 7.34-7.24 (m, 7H, Ar-H), 5.56 (m, 1H, Ar-CHO CO-), 5.36 (m, 1H, -SCH$_2$CH$_2$-), 4.67 (d, 1H, -CH$_2$OCO-), 4.43 (m, 1H, -CH$_2$OCO-), 3.15-3.05 (q, 15H, -SCH$_2$F$_3$ + 1H, -CH$_2$CHOCO-), 2.93-2.67 (23H, -CH$_2$CHO CO- + -CH$_2$SCH$_2$- + OOCCH$_2$CH$_2$COO), 1.07-1.04 (m, 16H, -SiCH$_2$-). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm, δ) 191.45, 171.59, 170.79, 165.10, 150.77, 139.30, 134.34, 130.39, 130.23, 129.40, 129.22, 128.50, 127.76, 127.51, 127.04, 126.74, 126.57, 125.76, 125.40, 124.83, 124.21, 123.65, 123.49, 122.62, 121.30, 112.94, 109.79, 71.23, 70.08, 46.28, 34.35, 34.04, 33.72, 33.17, 28.13, 27.76, 27.75, 26.78, 13.30, 12.54, 12.20. (M·Na)$^+$ calc. for C$_{68}$H$_{99}$O$_{19}$F$_{21}$Si$_8$Na 2233.46, Found 2233.46.
General procedure for synthesizing PS-(DPOSS)$_n$.
PS-(VPOSS)$_n$-$N_3$, 2 e.q. of 1-Thioglycerol to vinyl group and 0.03 eq of photoinitiator Irgacure 2959 were dissolve in THF. The solution was illuminated under 365 nm UV light for 10 min before precipitated into methanol/water 1:5. The products were collected by filtration.

| Sample       | $v_f^{\text{POSS}}$ | Phase structure | $d_1$ (nm) |
|--------------|----------------------|-----------------|------------|
| PS$_{135}$-(DPOSS)$_4$ | 0.32                 | LAM             | 20.9       |
| PS$_{83}$-(DPOSS)$_2$   | 0.28                 | LAM             | 14.4       |
| PS$_{83}$-(DPOSS)$_4$   | 0.43                 | LAM             | 16.1       |
| PS$_{27}$-(DPOSS)$_4$   | 0.70                 | HEX, inverse    | 10.5       |
| PS$_{27}$-(DPOSS)$_6$   | 0.77                 | disorder        | -          |
| PS$_{135}$-(HPOSS)$_4$  | 0.32                 | LAM             | 18.5       |
| PS$_{135}$-(HPOSS)$_5$  | 0.37                 | LAM             | 19.5       |
| PS$_{135}$-G2-(HPOSS)$_7$ | 0.45               | LAM             | 21.5       |
Figure S1. $^1$H NMR and MALDI-TOF spectra of DIBO-XPOSS-CHO.
Figure S2. $^1$H NMR spectra of $\text{PS}_{135^-}$-(XPOSS)$_n$-CHO.
Figure S3. $^1$H NMR spectra of PS$_{135}$-(XPOSS)$_n$-N$_3$. 
Figure S4. $^1$H NMR spectra of $\text{PS}_{135}^-$($\text{VPOSS})_n^-\text{N}_3$. 
Figure S5. $^1$H NMR spectra of PS$_{135}$-(HPOSS)$_n$. 
Figure S6. FT-IR spectra of PS$_{135}$-(XPOSS)$_n$-N$_3$, PS$_{135}$-(XPOSS)$_n$-CHO and their zoom-in spectra.
Figure S7. SAXS profiles of $\text{PS}_{135}-(\text{HPOSS})_n$, $\text{PS}_{135}-(\text{DPOSS})_n$, $\text{PS}_{135}-(\text{HPOSS})_3$, $\text{PS}_{83}-(\text{DPOSS})_n$ and $\text{PS}_{135}-(\text{DPOSS})_3$, $\text{PS}_{135}-(\text{DPOSS})_4$, and $\text{PS}_{27}-(\text{DPOSS})_n$. 
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