Supporting Information

Giant Molecules with Varying Geometric Features by Programming the Unit Sequence

Ze Yang,[1†] Zhongguo Liu,[1,2†] Shuai Wang,[1] Gang Li,[2*] and Xue-Hui Dong[1*]

[1]South China Advanced Institute for Soft Matter Science and Technology, School of Emergent Soft Matter, South China University of Technology, Guangzhou 510640, China

[2]Key Laboratory of Nanchang City for Green New Materials and Industrial Wastewater Treatment, Department of Ecology and Environment, Yuzhang Normal University, Nanchang 330103, China

1. Chemicals and Solvents

The following chemicals were used as received: octavinylPOSS (Hybrid Plastics), 2-Hydroxy-1-ethanethiol (Adamas, 98%), 1-butanethiol (Sigma, 93%), 1-octanethiol (Sigma, 93%), 1-dodecanethiol (Sigma, 93%), maleimide (Sigma, 95%), furan (Sigma, 98%), 1-thioglycerol (Sigma, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 98%, TCI America), diisopropyl azodicarboxylate (DIAD, 97%, TCI America), triphenylphosphine (PPh3, 97%, TCI America), tetrabromomethane (CBr_4, 98%, TCI America), thiourea (Sigma, 98%), sodium metabisulfiteanhydrous (Sigma, 98%), sodium sulfate (Na_2SO_4, Sigma, 93%), tetrahydrofuran (THF), triethylamine (TEA), toluene, petroleum ether (PE), ethyl acetate (EA), methanol (MeOH), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2).

2. Characterizations

Nuclear Magnetic Resonance (NMR). All ^{1}H NMR spectra were acquired in $CDCl_3$ using a Bruker 500 MHz NMR spectrometer. The spectra were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.27 ppm. ^{29}Si NMR spectra were acquired in $CDCl_3$ using a Bruker 99 MHz NMR spectrometer and referenced to tetramethylsilane (TMS) at δ 0.00 ppm.

Size exclusion chromatography (SEC). SEC analyses for polymeric chains were measured at 35 °C on a Tosoh HLC-8320 instrument equipped with three TSKgel columns (SuperH2000, SuperH3000, and SuperH4000) in series, a double flow type RI detector, and a UV-8320 UV detector. The eluting solvent is THF. The flow rate was 0.6 mL/min. Data acquisition was performed using EcoSEC software. And PS was used as the standard for molecular weight calculation.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS). All MALDI-TOF mass spectra were obtained on an UltrafleXtreme MALDI ToF mass spectrometer (Bruker Daltonics) equipped with a 1 kHz smart beam-II laser. trans-2-[3-(4-tert-Butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) was prepared in $CHCl_3$ (20 mg/mL) as matrix. The cationizing agent sodium trifluoroacetate was prepared in ethanol (10 mg/mL). The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in $CHCl_3$ at a concentration of 10 mg/mL. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity.

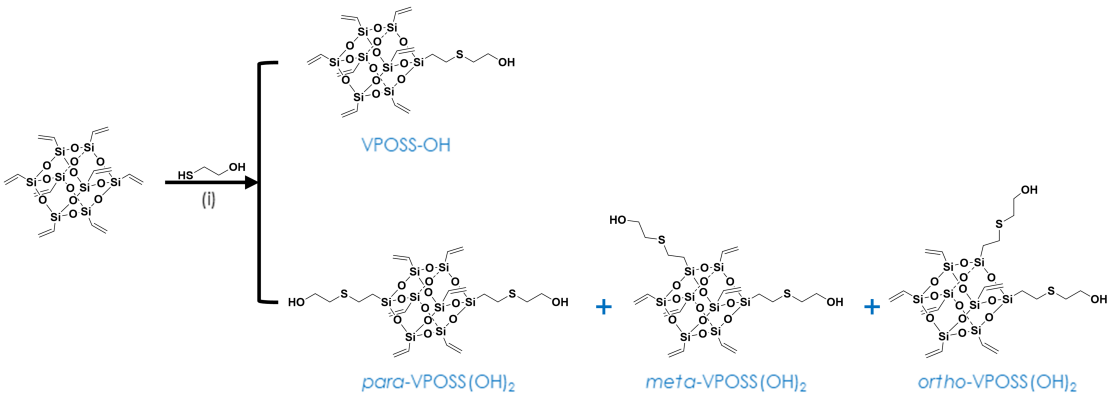
Small angle X-ray scattering (SAXS). SAXS experiments were performed on beamline BL16B1 at Shanghai Synchrotron Radiation (SSRF). The incident X-ray photon energy was 10 keV; the wavelength of the X-ray was 0.124 nm; the photo flux was 1×10^{11} phs/s. The beam size is smaller than 0.4×0.5 mm^2. Scattered X-rays were captured on a 2-dimensional Pilatus detector. The instrument was calibrated with diffraction patterns from silver behenate.

Recycling preparative SEC. Sample separation were performed on a LaboACE LC-5060 (Japan Analytical Industry Co., Ltd) instrument equipped with two JAIGEL-HR columns (2HR and 2.5HR) in series, a double flow type RI-700 LA detector, and a UV-4ch 800 LA detector. THF was used as eluent with a flow-rate of 10 mL/min. Crude polymers were dissolved in THF at a concentration of 50 mg/mL and filtered through a 0.45 μm PTFE syringe filter prior to inject. The data were monitored in real time by JAI scan software and the target fraction was collected manually.

3. Syntheses

3.1 Syntheses of building blocks with thiol or maleimide groups

a) VPOSS-OH and *para*-, *meta*-, and *ortho*-VPOSS(OH)$_2$



Scheme S1. Synthesis of octavinyl POSS with hydroxyl substituting groups: (i) 2-Hydroxy-1-ethanethiol, DMPA, THF, 25 °C, 365 nm × 50 min.

OctavinylPOSS (30.0 g, 47.4 mmol, 1.0 eq), 2-Hydroxy-1-ethanethiol (7.41 g, 94.8 mmol, 2.0 eq), and DMPA (120 mg, 0.47 mmol, 0.01 eq) were dissolved in 350 mL of THF, and irradiated with UV (365 nm) for 50 min. After removing solvent, the regio-isomers were isolated by silica gel column chromatography. A gradient of eluents EA/DCM (v/v from 1/20 to 1/4) was used to afford the products as white powders.

VPOSS-OH (9.0 g, yield: 26.7%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.14-5.87 (m, 21H, -C<u>H</u>=C<u>H$_2$</u>), 3.71 (t, J = 5.0

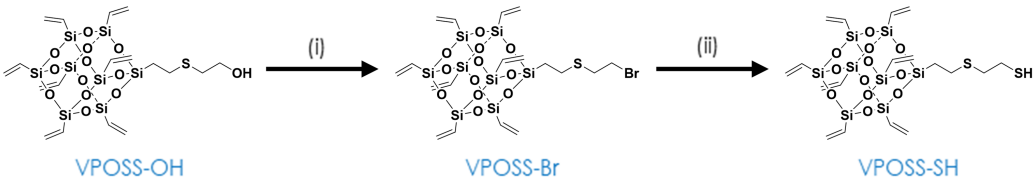
Hz, 2H, -C$\underline{H}_2$OH), 2.74 (t, 2H, -SiCH$_2$CH$_2$SC$\underline{H}_2$-), 2.66-2.64 (m, J = 7.3 Hz, 2H, -SiCH$_2$C$\underline{H}_2$SCH$_2$-), 1.09-1.06 (m, 2H, -SiC$\underline{H}_2$-).

***para*-VPOSS(OH)$_2$** (1.0 g, yield: 2.3%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 6.14-5.87 (m, 21H, -C$\underline{H}$=C$\underline{H}_2$), 3.70 (t, J = 5.0 Hz, 4H, -C$\underline{H}_2$OH), 2.73 (t, 4H, -SiCH$_2$CH$_2$SC$\underline{H}_2$-), 2.66-2.64 (m, J = 7.3 Hz, 4H, -SiCH$_2$C$\underline{H}_2$SCH$_2$-), 1.09-1.06 (m, 4H, -SiC$\underline{H}_2$-).

***meta*-VPOSS(OH)$_2$** (1.8 g, yield: 4.1%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 6.14-5.87 (m, 21H, -C$\underline{H}$=C$\underline{H}_2$), 3.70 (t, J = 5.0 Hz, 4H, -C$\underline{H}_2$OH), 2.73 (t, 4H, -SiCH$_2$CH$_2$SC$\underline{H}_2$-), 2.66-2.64 (m, J = 7.3 Hz, 4H, -SiCH$_2$C$\underline{H}_2$SCH$_2$-), 1.09-1.06 (m, 4H, -SiC$\underline{H}_2$-).

***ortho*-VPOSS(OH)$_2$** (2.7 g, yield: 6.2%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 6.14-5.87 (m, 21H, -C$\underline{H}$=C$\underline{H}_2$), 3.70 (t, J = 5.0 Hz, 4H, -C$\underline{H}_2$OH), 2.73 (t, 4H, -SiCH$_2$CH$_2$SC$\underline{H}_2$-), 2.66-2.64 (m, J = 7.3 Hz, 4H, -SiCH$_2$C$\underline{H}_2$SCH$_2$-), 1.09-1.06 (m, 4H, -SiC$\underline{H}_2$-).

b) VPOSS-SH



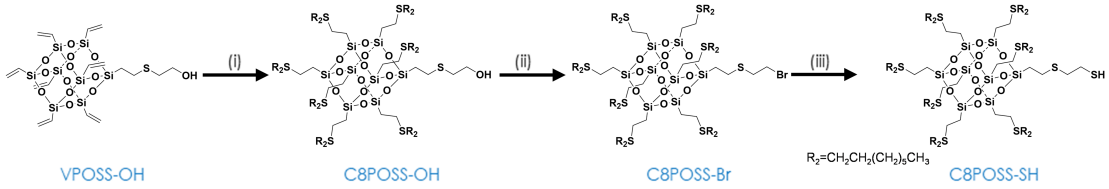
Scheme S2. Synthetic route of the VPOSS-SH: (i) CBr$_4$, PPh$_3$, CH$_2$Cl$_2$, 25 °C, 2 h; (ii) thiourea, EtOH, 70 °C, 12 h; sodium metabisulfite, CH$_2$Cl$_2$/H$_2$O, 70 °C, 4 h.

VPOSS-Br. VPOSS-OH (2.00 g, 2.8 mmol, 1.0 eq) was dissolved in 30 mL of CH$_2$Cl$_2$ in a 50 mL round-bottom flask. CBr$_4$ (1.39 g, 4.2 mmol, 1.5 eq) was added to the mixture. When completely dissolving, PPh$_3$ (1.10 g, 4.2 mmol, 1.5 eq) was slowly added. After string for 2 hours, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with PE/EA (10/1, v/v) as eluent to afford VPOSS-Br (1.74 g, yield: 80%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 6.15-5.85 (m, 21H, -C$\underline{H}$=C$\underline{H}_2$), 3.52 (t, 2H, -C$\underline{H}_2$Br), 2.64 (t, 2H, -SiCH$_2$CH$_2$SC$\underline{H}_2$-), 2.52 (t, 2H, -SiCH$_2$C$\underline{H}_2$SCH$_2$-), 1.05 (t, 2H, -SiC$\underline{H}_2$-).

VPOSS-SH. A solution of VPOSS-Br (1.40 g, 1.8 mmol, 1.0 eq) and thiourea (2.75g, 36.2 mmol, 20.1 eq) in methanol (20 mL) and tetrahydrofuran (20 mL) was heated at 70 °C for 12 h. The solvent was removed under vacuum, the solid

residue (the thiourea derivative) was dissolving in water (30 mL) and treated with sodium metabisulfite (6.88 g, 36.2 mmol, 20.1 eq) followed by CH_2Cl_2 (30 mL). The reaction mixture was heated at reflux for 4 h until the thiourea derivative had completely reacted as indicated by TLC. The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with CH_2Cl_2 2 × 40 mL, the combined organic phases were dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by silica gel column chromatography with PE/EA (10/1, v/v) as eluent to afford VPOSS-SH (0.85 g, yield: 63%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.15-5.85 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 2.64-2.78 (m, 6H, -C<u>H</u>$_2$SH, -SiCH$_2$C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.05 (t, 2H, -SiC<u>H</u>$_2$-).

c) C8POSS-SH and *para*-, *meta*-, and *ortho*-C8POSS-(SH)$_2$



Scheme S3. Synthetic route of the C8POSS-SH: (i) 1-octanethiol, DMPA, THF, 25 °C, 365 nm × 40 min; (ii) CBr_4, PPh_3, CH_2Cl_2, 25 °C, 2 h; (iii) thiourea, MeOH, 70 ℃, 12 h; sodium metabisulfite, CH_2Cl_2/H_2O, 70 ℃, 4 h.

C8POSS-OH. VPOSS-OH (2.00 g, 2.8 mmol, 1.0 eq), 1-octanethiol (4.11 g, 28.1 mmol, 10.0 eq), and DMPA (20.0 mg, 0.07 mmol, 0.03 eq) were dissolved in 20 mL of THF. After UV irradiation for 40 min, solvent was evaporated under vacuum. The residue was purified by silica gel chromatography with PE/EA (98/2) as eluent to afford the product as colorless oil liquid (3.50 g, yield: 72%).

C8POSS-Br. C8POSS-OH (3.70 g, 2.1 mmol, 1.0 eq) was dissolved in 20 mL of CH_2Cl_2 in a 50 mL round-bottom flask. CBr_4 (1.06 g, 3.2 mmol, 1.5 eq) was added to the mixture. When completely dissolving, PPh_3 (0.85 g, 3.2 mmol, 1.5 eq) was slowly added. After string for 2 hours, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with PE/EA (98/2, v/v) as eluent to afford C8POSS-Br (3.20 g, yield: 93%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 3.48 (m, 2H, -C<u>H</u>$_2$Br), 2.95 (m, 2H, -SiCH$_2$CH$_2$SC<u>H</u>$_2$CH$_2$Br), 2.49-2.69 (m, 30H, -SiCH$_2$C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.57 (m, 14H, -SCH$_2$C<u>H</u>$_2$-), 1.20-1.43 (m, 70H, -SCH$_2$CH$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$-), 1.02 (m, 16H, -SiC<u>H</u>$_2$-), 0.88 (t, 21H, -CH$_2$C<u>H</u>$_3$).

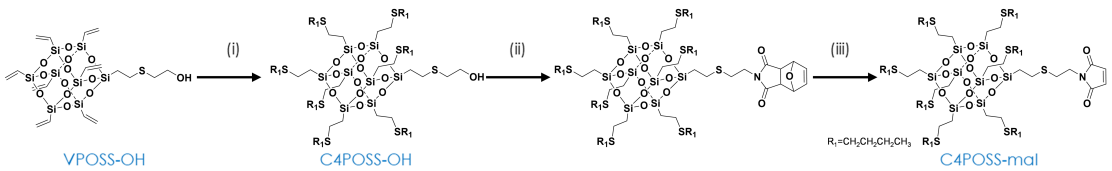
C8POSS-SH. A solution of C8POSS-Br (1.00 g, 0.56 mmol, 1.0 eq) and thiourea (0.85 g, 11.2 mmol, 20.0 eq) in

methanol (15 mL) and tetrahydrofuran (20 mL) was heated at 70 °C for 12 h. The solvent was removed under vacuum, the solid residue (the thiourea derivative) was dissolving in water (15 mL) and treated with sodium metabisulfite (2.11 g, 11.2 mmol, 20.0 eq) followed by CH_2Cl_2 (20 mL). The reaction mixture was heated at reflux for 4 h until the thiourea derivative had completely reacted as indicated by TLC. The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with dichloromethane 2 × 40 mL, the combined organic phases were dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by silica gel column chromatography with PE as eluent to afford C8POSS-SH (0.85g, yield: 88%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 2.67-2.78 (m, 4H, -C$\underline{H}_2$SH, -SiCH$_2$CH$_2$SC$\underline{H}_2$CH$_2$SH), 2.46-2.64 (m, 30H, -SiCH$_2$C$\underline{H}_2$SC$\underline{H}_2$-), 1.56 (m, 14H, -SCH$_2$C$\underline{H}_2$-), 1.19-1.41 (m, 70H, -SCH$_2$CH$_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$-), 1.00 (m, 16H, -SiC$\underline{H}_2$-), 0.87 (t, 21H, -CH$_2$C$\underline{H}_3$).

The syntheses of *para*-, *meta*-, and *ortho*-C8POSS-$(SH)_2$ follow the same protocol, except VPOSS-$(OH)_2$ was used instead of VPOSS-OH.

C8POSS-$(SH)_2$ (0.85g, yield: 95%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 2.67-2.78 (m, 8H, -C$\underline{H}_2$SH, -SiCH$_2$CH$_2$SC$\underline{H}_2$CH$_2$SH), 2.46-2.64 (m, 28H, -SiCH$_2$C$\underline{H}_2$SC$\underline{H}_2$-), 1.56 (m, 14H, -SCH$_2$C$\underline{H}_2$-), 1.19-1.41 (m, 60H, -SCH$_2$CH$_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$-), 1.00 (m, 16H, -SiC$\underline{H}_2$-), 0.87 (t, 18H, -CH$_2$C$\underline{H}_3$).

d) C4POSS-mal, C8POSS-mal and C12POSS-mal



Scheme S4. Synthetic route of the C4POSS-mal: (i) 1-butanethiol, DMPA, THF, 25 °C, 365 nm × 40 min; (ii) Furan-protected-maleimide, DIAD, PPh_3, THF, 25 °C, 12 h; (iii) Toluene, 120 °C, 4 h.

C4POSS-OH. VPOSS-OH (2.00 g, 2.8 mmol, 1.0 eq), 1-butanethiol (2.54 g, 28.1 mmol, 10.0 eq), and DMPA (20.0 mg, 0.07 mmol, 0.03 eq) were dissolved in 20 mL of THF. After UV irradiation for 40 min, solvent was evaporated under vacuum. The residue was purified by silica gel chromatography with PE/EA (5/1, v/v) as eluent to afford the product as colorless oil liquid (2.90 g, yield: 77%).

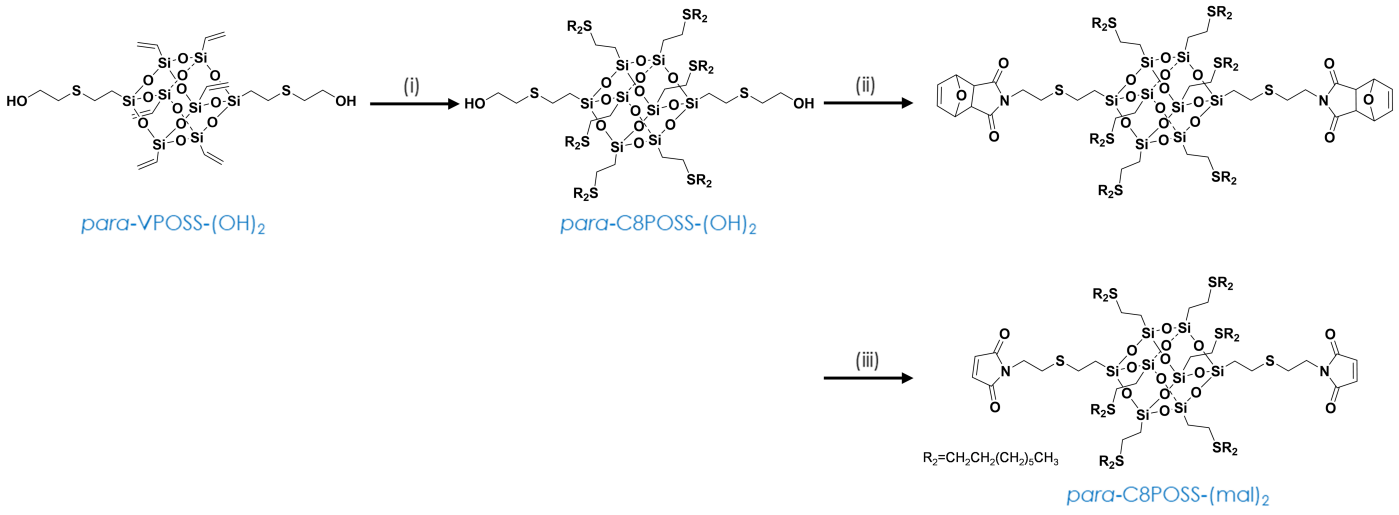
C4POSS-fumal. C4POSS-OH (2.90 g, 2.16 mmol, 1.0 eq), furan-protected-maleimide (0.46 g, 2.81 mmol, 1.3 eq), and

triphenylphosphine (0.74 g, 2.81 mmol, 1.3 eq) were added to a round-bottom flask with dry THF (30 mL), and purged with nitrogen. The reaction mixture was stirred and diisopropyl azodicarboxylate (DIAD, 0.57 g, 2.81 mmol, 1.3 eq) was added dropwise. The solution was allowed to stir for 12 h. After the reaction, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography with PE/EA (14/1, v/v) as eluent to afford the product as colorless oil liquid (2.90 g, yield: 80%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.51 (s, 2H, -C<u>H</u>=C<u>H</u>-), 5.27 (s, 2H, -CH(-O-)C-), 3.65 (m, 2H, -C<u>H</u>$_2$N), 2.86 (s, 2H, -CH(-C=O)CH-), 2.48-2.71 (m, 32H, -SiCH$_2$C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.56 (m, 14H, -SCH$_2$C<u>H</u>$_2$CH$_2$-), 1.42 (m, 14H, -SCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$-), 1.02 (m, 16H, -SiC<u>H</u>$_2$-), 0.92 (t, 21H, -CH$_2$C<u>H</u>$_3$).

C4POSS-mal. C4POSS-fumal (2.50 g, 1.68 mmol, 1.0 eq) was dissolved in 20 mL of toluene. The mixture was stirred in an oil bath at 120 ºC under argon flow for about 6h. TLC showed the reaction was complete. After cooling to room temperature, toluene was evaporated under vacuum and the crude product was purified by silica gel column chromatography with PE/EA (95/5, v/v) as eluent to afford C4POSS-mal (2.30 g, yield: 96%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.70 (s, 2H, -C<u>H</u>=C<u>H</u>-), 3.70 (m, 2H, -C<u>H</u>$_2$N), 2.48-2.77 (m, 32H, -SiCH$_2$C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.56 (m, 14H, -SCH$_2$C<u>H</u>$_2$CH$_2$-), 1.40 (m, 14H, -SCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$-), 1.01 (m, 16H, -SiC<u>H</u>$_2$-), 0.92 (t, 21H, -CH$_2$C<u>H</u>$_3$).

The syntheses of C8POSS-mal and C12POSS-mal follow the same protocol, except 1-octanethiol and 1-dodecanethiol were used instead of 1-butanethiol.

e) *para*-C8POSS-(mal)$_2$, *meta*-, and *ortho*-C4/C8/C12POSS-(mal)$_2$



Scheme S5. Synthetic route of the *para*-C8POSS-(mal)$_2$: (i) 1-octanethiol, DMPA, THF, 25 °C, 365 nm × 40 min; (ii) Furan-protected-maleimide, DIAD, PPh$_3$, THF, 25°C, 12 h; (iii) Toluene, 120 °C, 4 h.

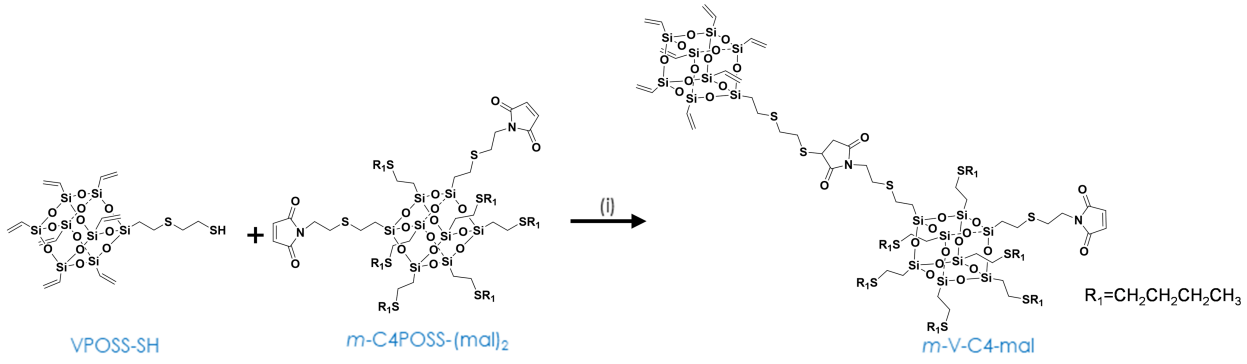
***para*-C8POSS-(OH)$_2$.** *para*-VPOSS-(OH)$_2$ (2.50 g, 3.17 mmol, 1.0 eq), 1-octanethiol (2.57 g, 28.5 mmol, 9.0 eq), and DMPA (20.0 mg, 0.07 mmol, 0.02 eq) were dissolved in 20 mL of THF. After UV irradiation for 40 min, solvent was evaporated under vacuum. The residue was purified by silica gel chromatography with PE/EA (93/7) as eluent to afford the product as colorless oil liquid (4.57 g, yield: 87%).

***para*-C8POSS-(mal)$_2$.** *para*-C8POSS-(OH)$_2$ (8.34 g, 5.0 mmol, 1.0 eq), furan-protected-maleimide (3.80 g, 15.0 mmol, 3.0 eq), and triphenylphosphine (3.93 g, 15.0 mmol, 3.0 eq) were added to a round-bottom flask with dry THF (50 mL), and purged with nitrogen. The reaction mixture was stirred and diisopropyl azodicarboxylate (DIAD, 3.03 g, 15.0 mmol, 1.0 eq) was added dropwise. The solution was allowed to stir for 12 h. After the reaction, the solvent was removed under reduced pressure and 80 mL of toluene was added. The mixture was stirred and refluxed at 120 ºC for about 6 h. TLC showed the reaction was complete. After cooling to room temperature, toluene was evaporated under vacuum and the crude product was purified by silica gel column chromatography with PE/EA (97/3, v/v) as eluent to afford *para*-C8POSS-(mal)$_2$ (2.98g, yield: 72%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.71 (s, 4H, -C<u>H</u>=C<u>H</u>-), 3.71 (m, 4H, -C<u>H</u>$_2$N), 2.73 (m, 4H, -SiCH$_2$CH$_2$SC<u>H</u>$_2$ CH$_2$N -), 2.48-2.67 (m, 28H, -SiCH$_2$C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.56 (m, 12H, -SCH$_2$C<u>H</u>$_2$-), 1.22-1.40 (m, 60H, -SCH$_2$CH$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$-), 1.01 (m, 16H, -SiC<u>H</u>$_2$-), 0.88 (t, 18H, -CH$_2$C<u>H</u>$_3$).

The syntheses of *meta*-, and *ortho*-C4/C8/C12POSS-(mal)$_2$ follow the same protocol, except *meta*-VPOSS-(OH)$_2$ and *ortho*-VPOSS-(OH)$_2$ were used instead of *para*-VPOSS-(OH)$_2$, 1-butanethiol and 1-dodecanethiol were used instead of 1-octanethiol.

3.2 Synthesis of alternating multiblock giant molecules with *meta*-configuration

a) *meta*-V-C4-mal, *meta*-V-C8-mal and *meta*-V-C12-mal

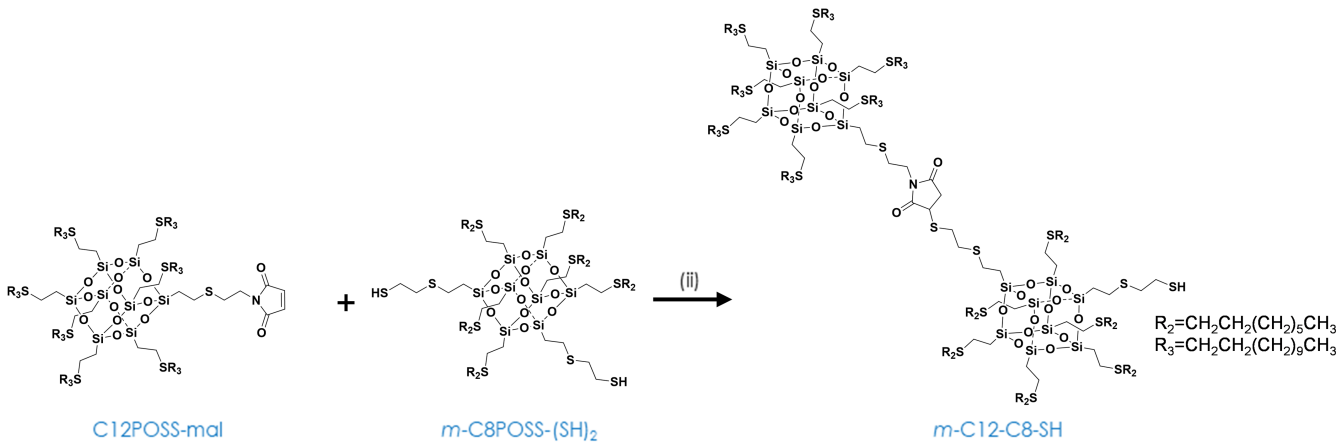


Scheme S6. Synthetic route of the *meta*-V-C4-mal: (i) TEA, $CHCl_3$, 25 °C, 8 h.

***meta*-V-C4-mal.** The VPOSS-SH (390 mg, 0.54 mmol, 1.0 eq) and *meta*-C4POSS-(mal)$_2$ (1.04 g, 0.70 mmol, 1.3 eq) were dissolved in 20 mL of $CHCl_3$ in a 25 mL round-bottom flask, TEA (0.1 mL, 0.72 mmol) was added to the solution and the mixture was stirred for about 10 h. The reaction mixture was quenched with 15 mL water and washed with 10 mL saturated $NaHCO_3$ (aq.). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude product which was purified by recycling preparative SEC to give the product as colorless oil liquid (620 mg, yield: 52%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.71 (s, 2H, -C<u>H</u>=C<u>H</u>-), 5.87-6.14 (m, 21H, C<u>H</u>$_2$=C<u>H</u>-), 3.80 (dd, 1H, -SC<u>H</u>(C=O)CH$_2$-), 3.70 (t, 4H, -NC<u>H</u>$_2$CH$_2$-), 3.17, 2.95 (m, 2H, -CHC<u>H</u>$_2$(C=O)-), 2.83 (m, 2H, -SCH$_2$C<u>H</u>$_2$S-), 2.48-2.77 (m, 36H, -C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.56 (m, 12H, -SCH$_2$C<u>H</u>$_2$-), 1.40 (m, 12H, -SCH$_2$CH$_2$C<u>H</u>$_2$-), 1.02 (m, 18H, -SiC<u>H</u>$_2$-), 0.92 (t, 18H, -CH$_2$C<u>H</u>$_3$).

The syntheses of *meta*-V-C8-mal and *meta*-V-C12-mal follow the same protocol, except *meta*-C8POSS-(mal)$_2$ and *meta*-C12POSS-(mal)$_2$ were used instead of *meta*-C4POSS-(mal)$_2$.

b) *meta*-C12-C8-SH, *meta*-C8-C8-SH and *meta*-C4-C8-SH



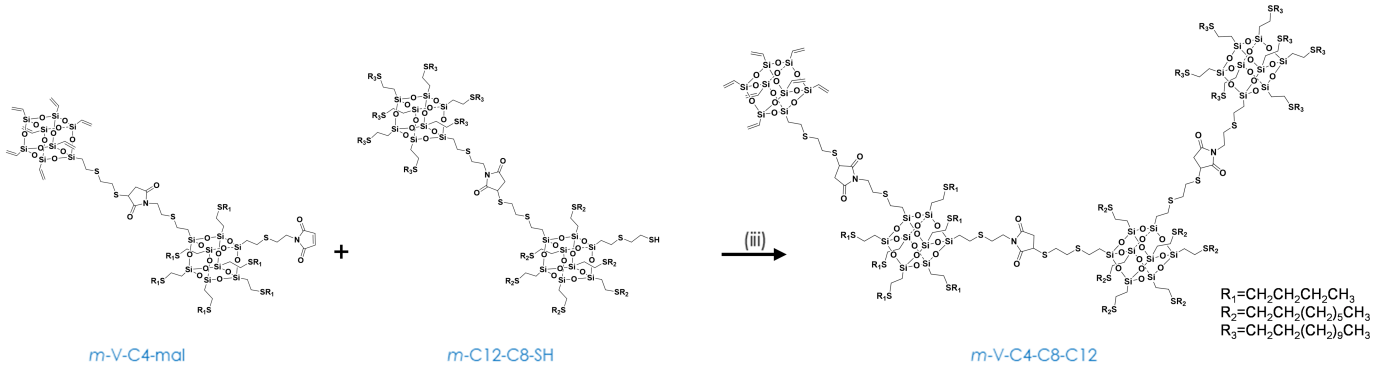
Scheme S7. Synthetic route of the *meta*-C12-C8-SH: (ii) TEA, $CHCl_3$, 25 °C, 8 h.

***meta*-C12-C8-SH.** The C12POSS-mal (300 mg, 0.14 mmol, 1.0 eq) and *meta*-C8POSS-(SH)$_2$ (305 mg, 0.18 mmol, 1.3 eq) were dissolved in 20 mL of dry $CHCl_3$ in a 25 mL round-bottom flask, TEA (0.1 mL, 0.72 mmol, 5.1 eq) was added dropwise to the solution and the mixture was stirred for about 10 h. The reaction mixture was quenched with 15 mL water and washed with 10 mL saturated $NaHCO_3$ (aq.). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude product which was purified by recycling preparative SEC to give the product as colorless oil liquid (250 mg, yield: 47%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 3.82 (dd, 1H, -

SC<u>H</u>(C=O)C<u>H</u>$_2$-), 3.70 (t, 2H, -NC<u>H</u>$_2$C<u>H</u>$_2$-), 3.17, 2.98 (m, 2H, -CHC<u>H</u>$_2$(C=O)-), 2.83 (m, 2H, -SCH$_2$C<u>H</u>$_2$S-), 2.45-2.80 (m, 66H, -C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.57 (m, 26H, -SCH$_2$C<u>H</u>$_2$-), 1.19-1.42 (m, 186H, -SCH$_2$CH$_2$C<u>H</u>$_2$-), 1.02 (m, 32H, -SiC<u>H</u>$_2$-), 0.88 (t, 39H, -CH$_2$C<u>H</u>$_3$).

The syntheses of *meta*-C8-C8-SH and *meta*-C4-C8-SH follow the same protocol, except C8POSS-mal and C4POSS-mal were used instead of C12POSS-mal.

c) *meta*-V-(C4-C8-C12), *meta*-V-C8$_3$ and *meta*-V-(C12-C8-C4)

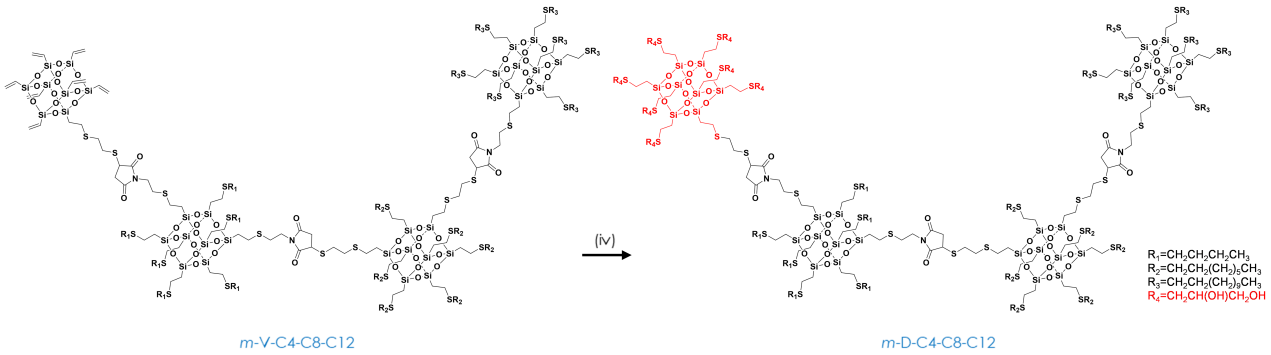


Scheme S8. Synthetic route of the *meta*-V-(C4-C8-C12): (iii) TEA, CHCl$_3$, 25 °C, 8 h.

***meta*-V-(C4-C8-C12).** The *meta*-C12-C8-SH (130 mg, 0.03 mmol, 1.0 eq) and *meta*-V-C4-mal (92.2 mg, 0.04 mmol, 1.3 eq) were dissolved in 10 mL of CHCl$_3$ in a 25 mL round-bottom flask, TEA (0.1 mL, 0.72 mmol, 24.0 eq) was added dropwise to the solution and the mixture was stirred for about 10 h. The reaction mixture was quenched with 15 mL water and washed with 10 mL saturated NaHCO$_3$ (aq.). The combined organic layer was dried with anhydrous Na$_2$SO$_4$ and the solvent was evaporated to afford the crude product which was purified by recycling preparative SEC to give the product as colorless oil liquid (110 mg, yield: 54%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm, δ): 5.87-6.14 (m, 21H, C<u>H</u>$_2$=C<u>H</u>-), 3.82 (m, 3H, -SC<u>H</u>(C=O)C<u>H</u>$_2$-), 3.70 (t, 6H, -NC<u>H</u>$_2$C<u>H</u>$_2$-), 3.17, 2.97 (m, 6H, -CHC<u>H</u>$_2$(C=O)-), 2.83 (m, 6H, -SCH$_2$C<u>H</u>$_2$S-), 2.46-2.77 (m, 100H, -C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.57 (m, 38H, -SCH$_2$C<u>H</u>$_2$-), 1.22-1.46 (m, 198H, -SCH$_2$CH$_2$C<u>H</u>$_2$-), 1.02 (m, 50H, -SiC<u>H</u>$_2$-), 0.88 (t, 57H, -CH$_2$C<u>H</u>$_3$).

The syntheses of *meta*-V-C8$_3$ and *meta*-V-(C12-C8-C4) follow the same protocol, except *meta*-C8-C8-SH and *meta*-C4-C8-SH were used instead of *meta*-C12-C8-SH, *meta*-V-C8-mal and *meta*-V-C12-mal were used instead of *meta*-V-C4-mal.

d) *meta*-D-(C4-C8-C12), *meta*-D-C8$_3$ and *meta*-D-(C12-C8-C4)



Scheme S9. Synthetic route of the *meta*-D-(C4-C8-C12): (iv) 1-thioglycerol, DMPA, THF, 25 °C, 365 nm ×50 min.

***meta*-D-(C4-C8-C12).** *meta*-V-(C4-C8-C12) (100 mg, 0.02 mmol, 1.0 eq), 15.0 eq of 1-thioglycerol and 0.03 eq of DMPA were dissolve in 3 mL of THF. The solution was illuminated under 365 nm UV light in a UV reactor for 50 min. The solution is concentrated and purified by recycling preparative SEC to give the product as colorless oil liquid (78 mg, yield: 70%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 3.52-3.88 (m, 30H, -C<u>H</u>(OH)C<u>H$_2$</u>(OH), -SC<u>H</u>(C=O)CH$_2$-, -NC<u>H$_2$</u>CH$_2$-,), 3.17, 2.97 (m, 6H, -CHC<u>H$_2$</u>(C=O)-), 2.83 (m, 6H, -SCH$_2$C<u>H$_2$</u>S-), 2.46-2.77 (m, 100H, -C<u>H$_2$</u>SC<u>H$_2$</u>-), 1.57 (m, 38H, -SCH$_2$C<u>H$_2$</u>-), 1.22-1.46 (m, 198H, -SCH$_2$CH$_2$C<u>H$_2$</u>-), 1.02 (m, 50H, -SiC<u>H$_2$</u>-), 0.88 (t, 57H, -CH$_2$C<u>H$_3$</u>).

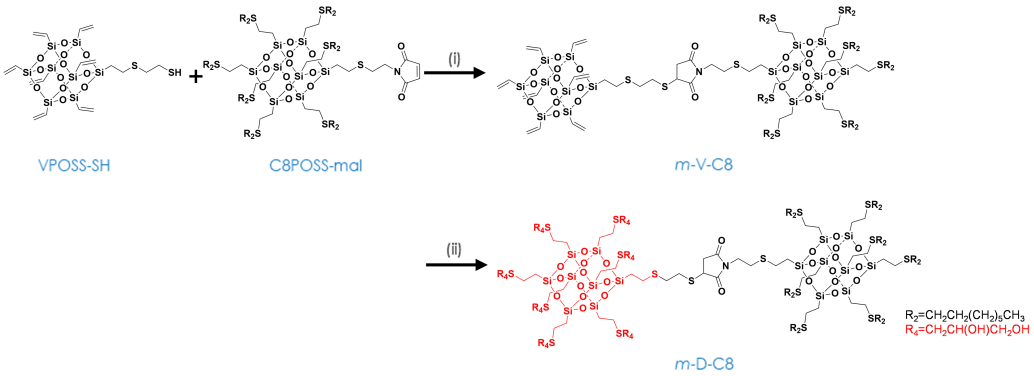
The syntheses of *meta*-D-C8$_3$ and *meta*-D-(C12-C8-C4) follow the same protocol, except *meta*-V-C8$_3$ and *meta*-V-(C12-C8-C4) were used instead of *meta*-(C4-C8-C12).

3.3 Synthesis of *para*-, *ortho*-D-(C*x*-C*y*-C*z*)

Their different regio-configurations (*para*-, *ortho*-D-(C*x*-C*y*-C*z*)) were synthesized with corresponding building block following the same protocol as *meta*-D-(C*x*-C*y*-C*z*).

3.4 Synthesis of *meta*-D-C8$_n$

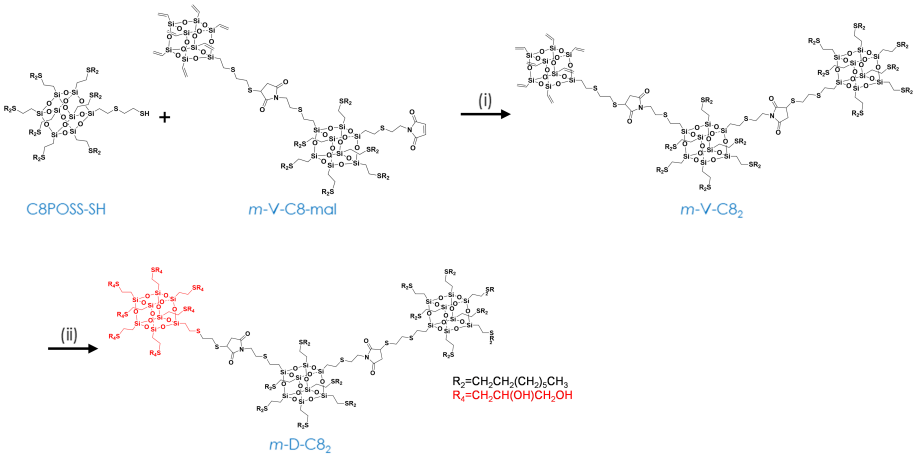
a) *meta*-D-C8



Scheme S10. Synthetic route of the *meta*-D-C8: (i) TEA, $CHCl_3$, 25 °C, 8 h; (ii) 1-thioglycerol, DMPA, THF, 25 °C, 365 nm ×50 min.

***meta*-D-C8.** *meta*-V-C8 (100 mg, 0.04 mmol), 15.0 eq of 1-thioglycerol and 0.03 eq of DMPA were dissolve in 3 mL of THF. The solution was illuminated under 365 nm UV light in a UV reactor for 50 min. The solution is concentrated and purified by recycling preparative SEC to give the product as colorless oil liquid (60 mg, yield: 46%).

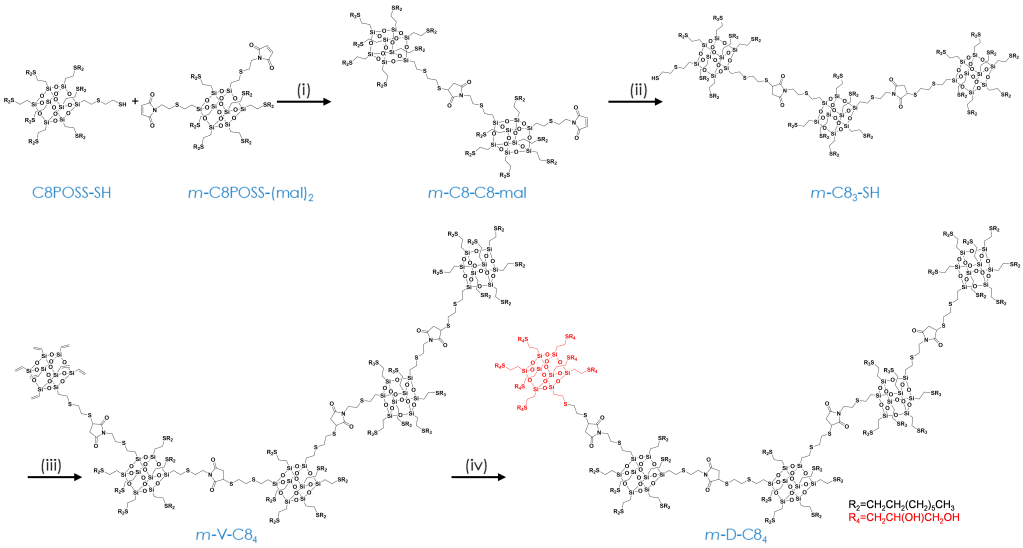
b) *meta*-D-C8$_2$



Scheme S11. Synthetic route of the *meta*-D-C8$_2$: (i) TEA, $CHCl_3$, 25 °C, 8 h; (ii) 1-thioglycerol, DMPA, THF, 25 °C, 365 nm ×50 min.

***meta*-D-C8$_2$.** *meta*-V-C8$_2$ (80 mg, 0.02 mmol), 15.0 eq of 1-thioglycerol and 0.03 eq of DMPA were dissolve in 3 mL of THF. The solution was illuminated under 365 nm UV light in a UV reactor for 50 min. The solution is concentrated and purified by recycling preparative SEC to give the product as colorless oil liquid (40 mg, yield: 43%).

b) *meta*-D-C8$_4$



Scheme S12. Synthetic route of the *meta*-D-C8$_4$: (i) TEA, $CHCl_3$, 25 °C, 8 h; (ii) *meta*-C8POSS-(SH)$_2$, TEA, $CHCl_3$, 25 °C, 8 h; (iii) *meta*-VPOSS-C8POSS-mal, TEA, $CHCl_3$, 25 °C, 8 h; (iv)1-thioglycerol, DMPA, THF, 25 °C, 365 nm ×50 min.

***meta*-D-C8$_4$.** *meta*-V-C8$_4$ (60 mg, 0.01 mmol, 1.0 eq), 15.0 eq of 1-thioglycerol and 0.03 eq of DMPA were dissolve in 3 mL of THF. The solution was illuminated under 365 nm UV light in a UV reactor for 50 min. The solution is concentrated and purified by recycling preparative SEC to give the product as colorless oil liquid (20 mg, yield: 30%).

4. Equation and calculations

4.1 Volume fraction of CPOSS (f_C).

The volume fraction of CPOSS (f_C) can be calculated by Eq. S1:

$$f_C = \frac{M_C/\rho_C}{M_C/\rho_C + M_D/\rho_D} \qquad \text{(S1)}$$

where M_D is the molecular weight of DPOSS, M_C is the molecular weight of CPOSS block, ρ_D and ρ_C are the density of DPOSS and CPOSS, respectively. The density of DPOSS is measured to be around 1.43 g/cm^3, and the density of CPOSS is estimated to be around 1.1 g/cm^3 (assuming the density of CPOSS is similar to that of BPOSS, *i.e.*, POSS with seven isobutyl groups).[1]

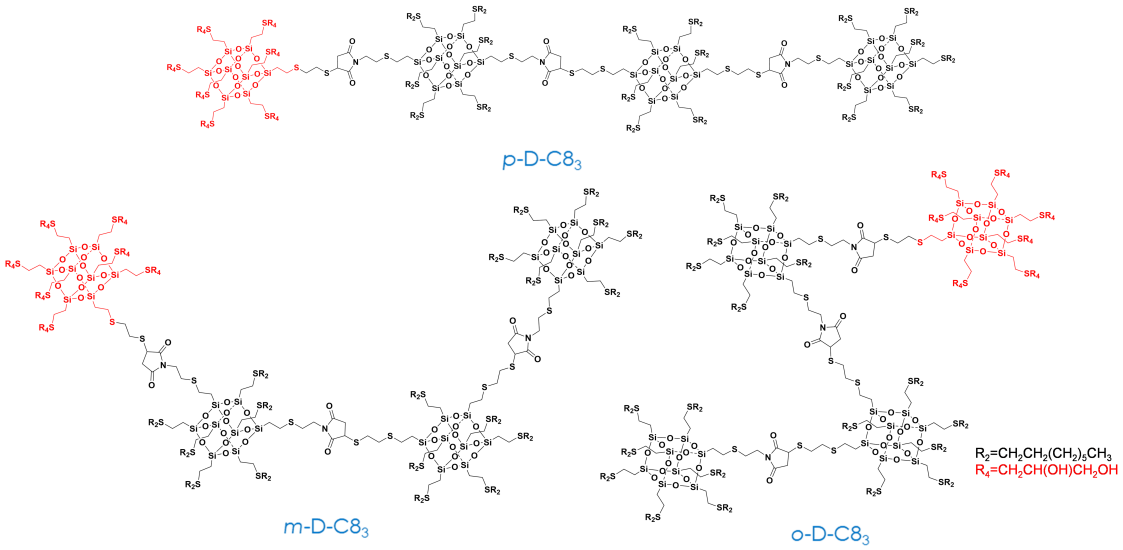
4.2 Characteristic dimension of the phase (*a*).

The dimension of the phase (*a*) refers to lamellar periodicities (for LAM), inter-column distances (for HEX). It can be calculated from domain spacing (*d*) accordingly.

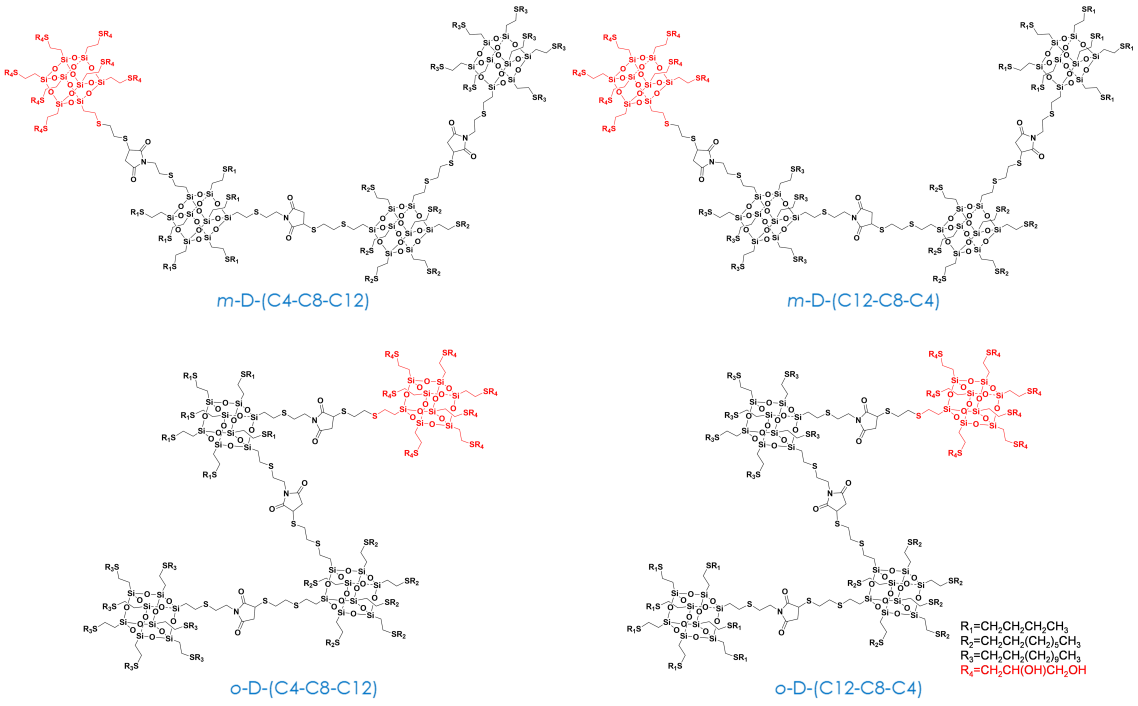
$$a = d \qquad \text{for LAM}$$

$$a = 2d/\sqrt{3} \qquad \text{for HEX}$$

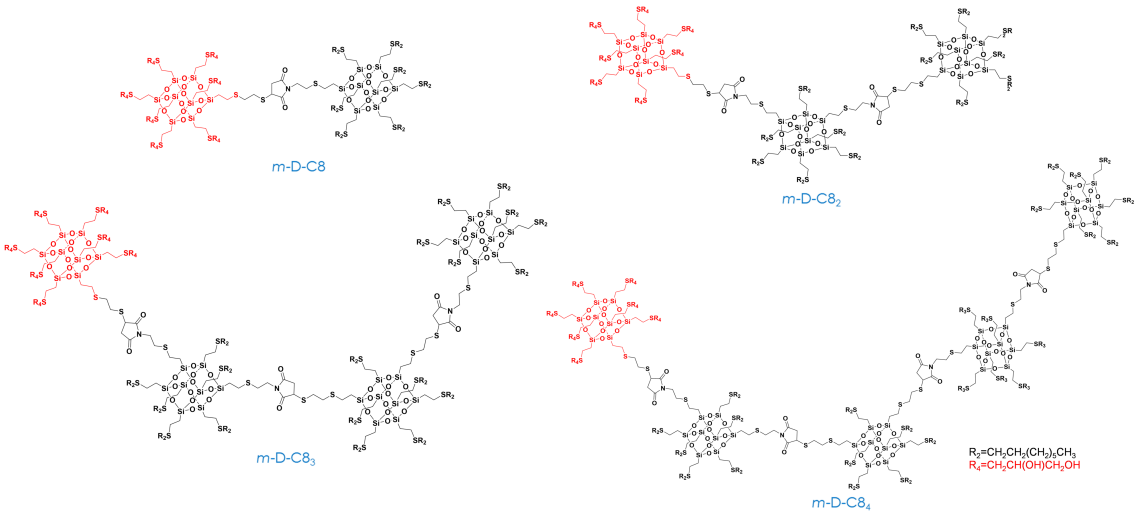
5. Supplementary Schemes and Figures



Scheme S13. Amphiphilic giant molecules D-C8$_3$ with *para*-, *meta*-, and *ortho*-configuration.



Scheme S14. Amphiphilic giant molecules D-(C4-C8-C12) and D-(C12-C8-C4) with *meta*-, and *ortho*-configuration.



Scheme S15. Amphiphilic giant molecules *meta*-D-C8, *meta*-D-C8$_2$, *meta*-D-C8$_3$ and *meta*-D-C8$_4$.

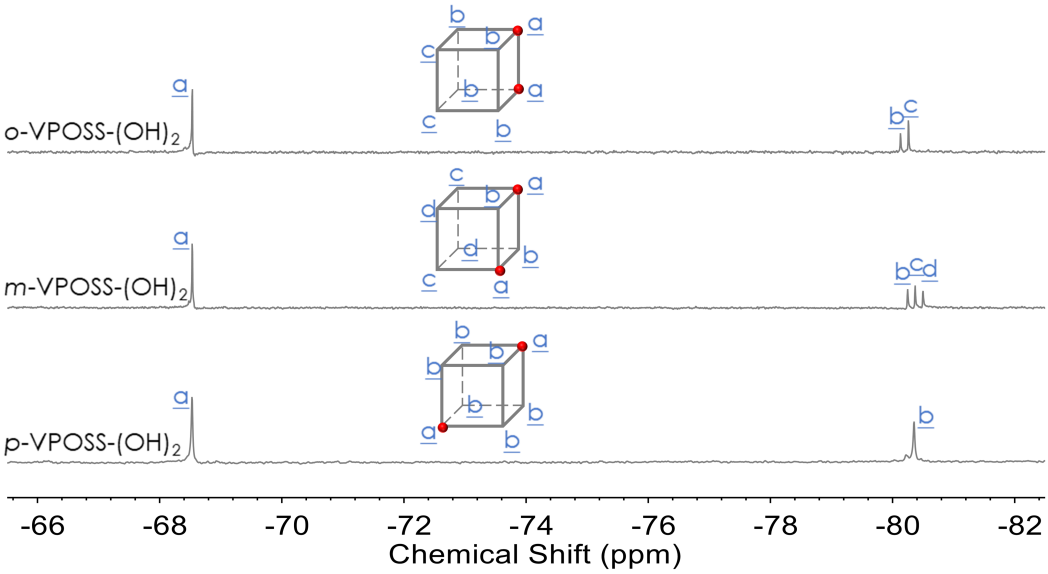


Figure S1. ^{29}Si NMR spectra of VPOSS-(OH)$_2$ with *para*-, *meta*-, and *ortho*-configuration. Asterisks denote signals from $CDCl_3$.

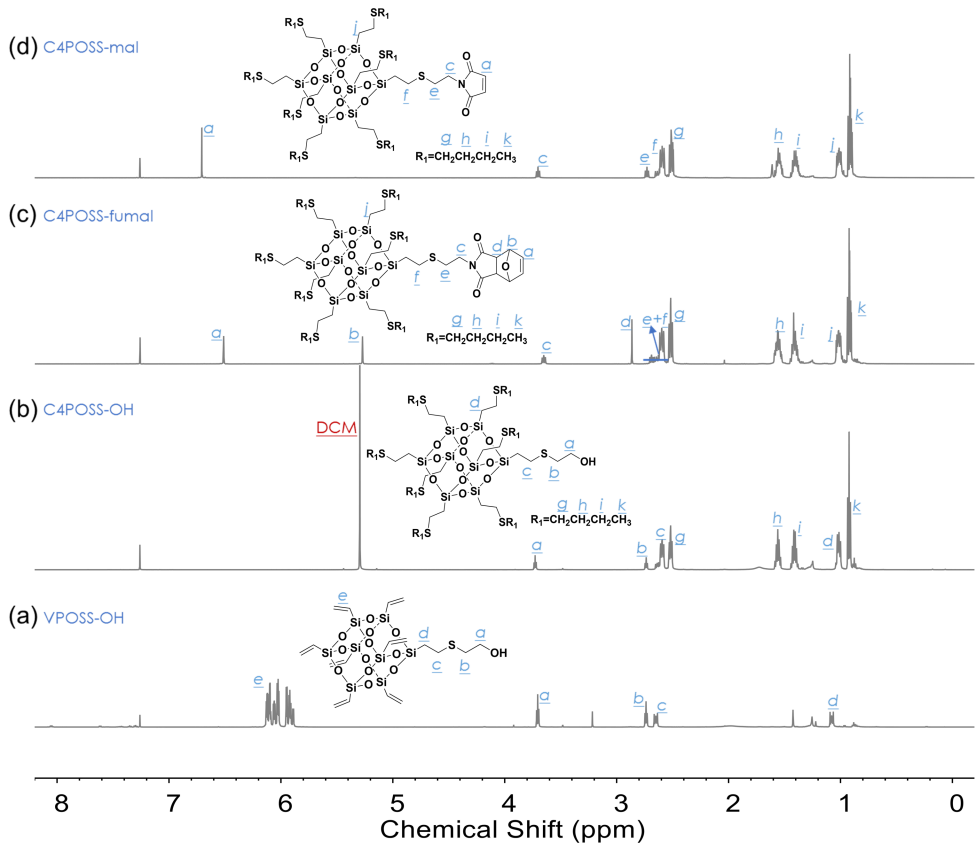


Figure S2. ^{1}H NMR spectra of VPOSS-OH (a), C4POSS-OH (b), C4POSS-fumal (c), C4POSS-mal (d). Take *meta*-configuration as an example. Asterisks denote signals from $CDCl_3$.

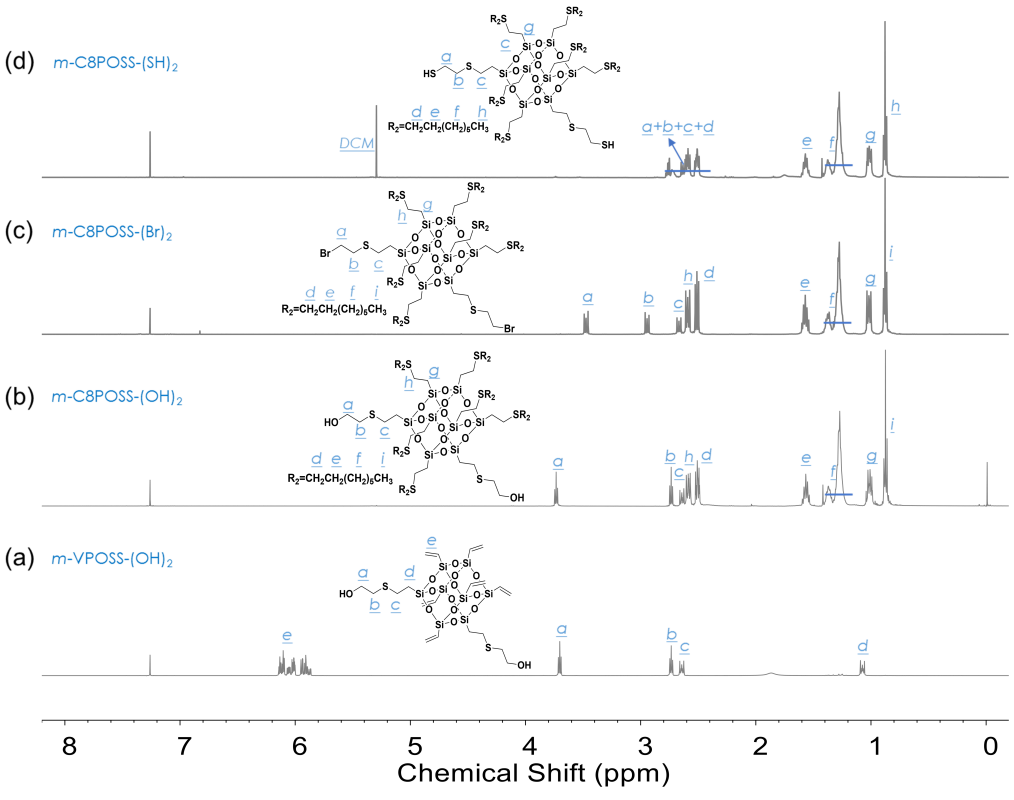


Figure S3. ^{1}H NMR spectra of *meta*-VPOSS-$(OH)_2$ (a), *meta*-C8POSS-$(OH)_2$ (b), *meta*-C8POSS-$(Br)_2$ (c), *meta*-C8POSS-$(SH)_2$ (d). Take *meta*-configuration as an example. Asterisks denote signals from $CDCl_3$.

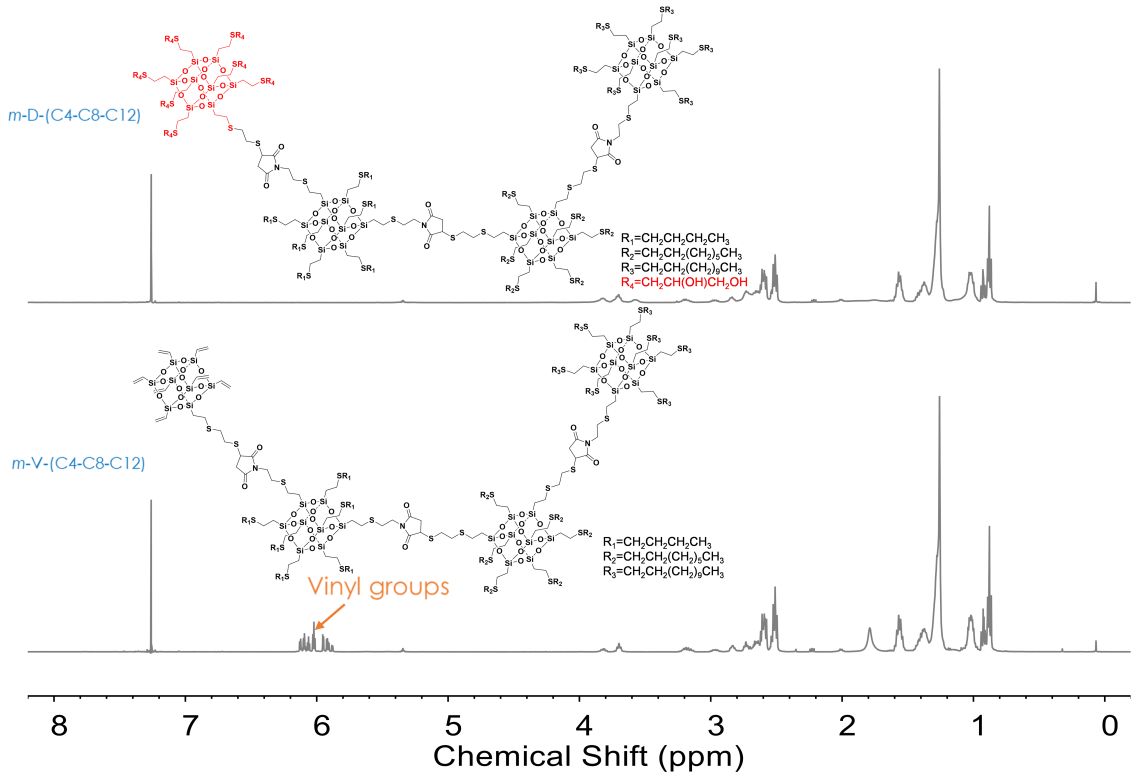


Figure S4. ^{1}H NMR spectra of *meta*-V-(C4-C8-C12) and *meta*-D-(C4-C8-C12). Take *meta*-configuration as an example. Asterisks denote signals from $CDCl_3$.

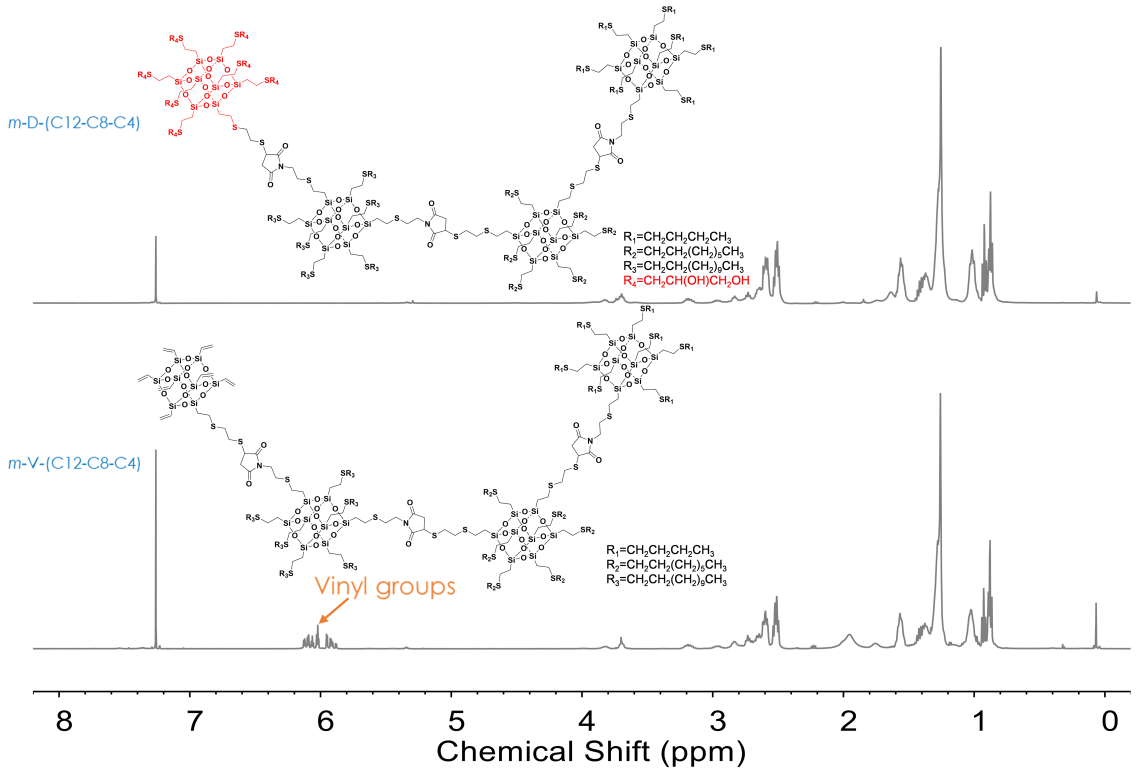


Figure S5. ^{1}H NMR spectra of *meta*-V-(12-C8-C4) and *meta*-D-(C12-C8-C4). Take *meta*-configuration as an example. Asterisks denote signals from $CDCl_3$.

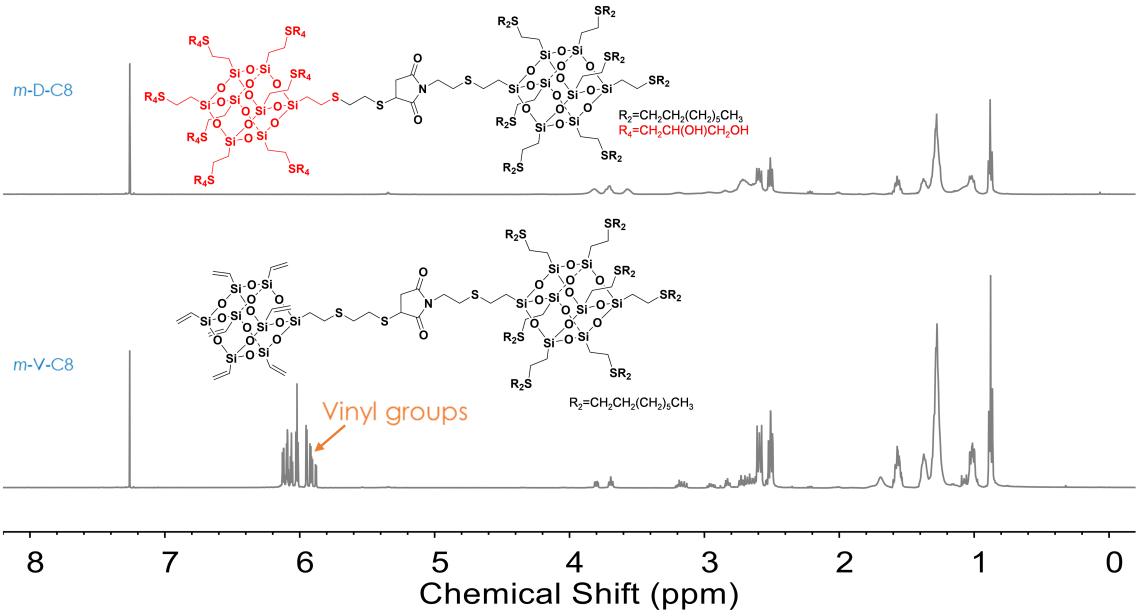


Figure S6. ^{1}H NMR spectra of *meta*-V-C8 and *meta*-D-C8. Asterisks denote signals from $CDCl_3$.

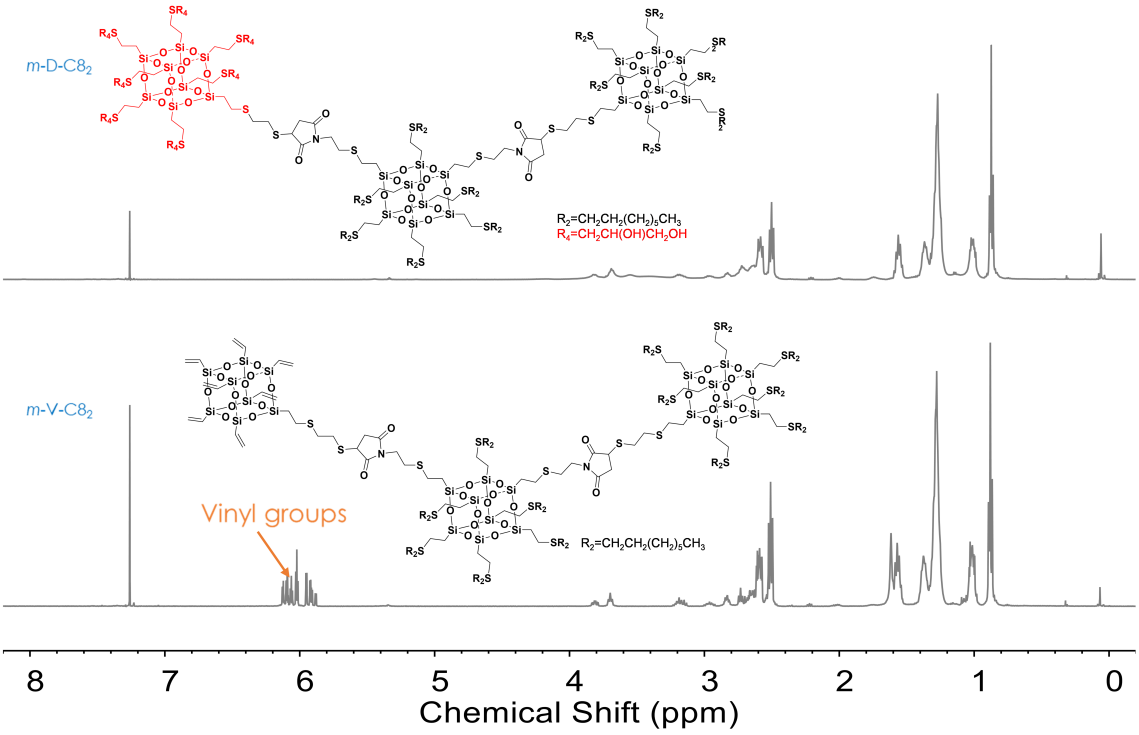


Figure S7. ^{1}H NMR spectra of *meta*-V-$C8_2$ and *meta*-D-$C8_2$. Asterisks denote signals from $CDCl_3$.

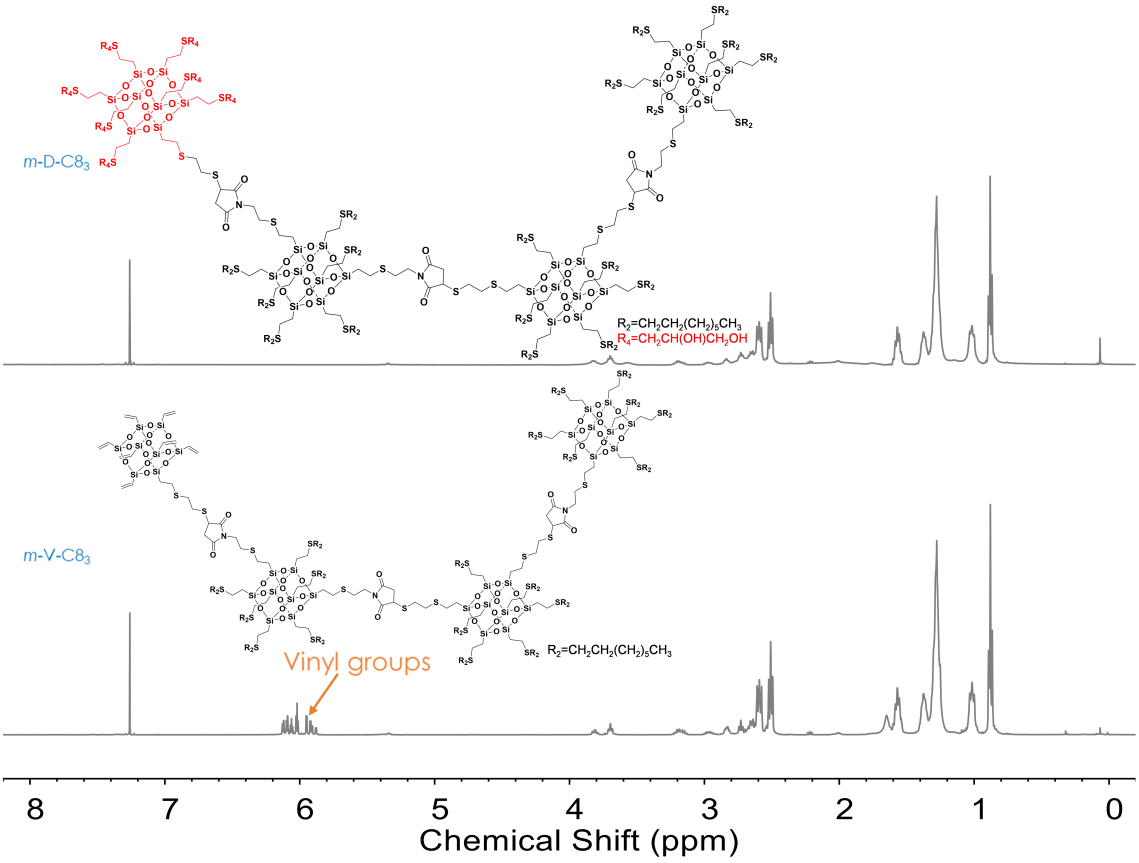


Figure S8. ^{1}H NMR spectra of *meta*-V-C8$_3$ and *meta*-D-C8$_3$. Asterisks denote signals from $CDCl_3$.

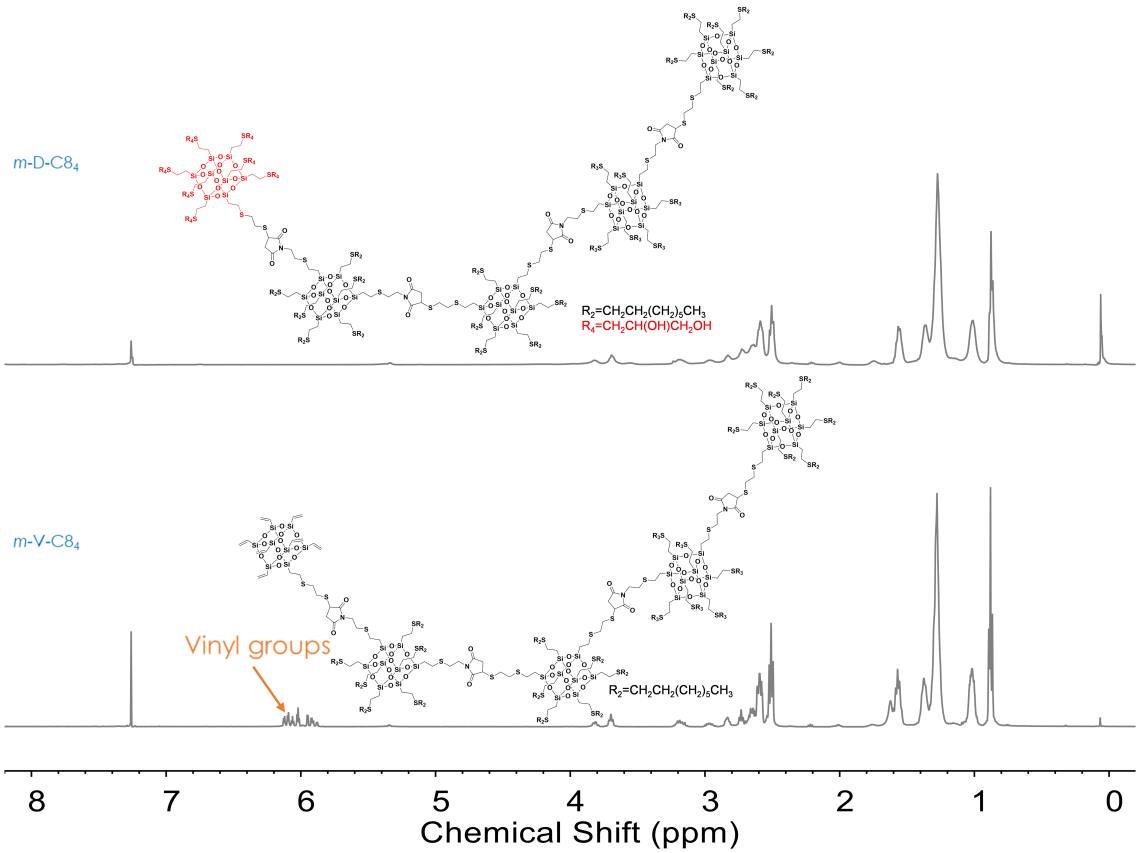


Figure S9. ^{1}H NMR spectra of *meta*-V-C8$_4$ and *meta*-D-C8$_4$. Asterisks denote signals from $CDCl_3$.

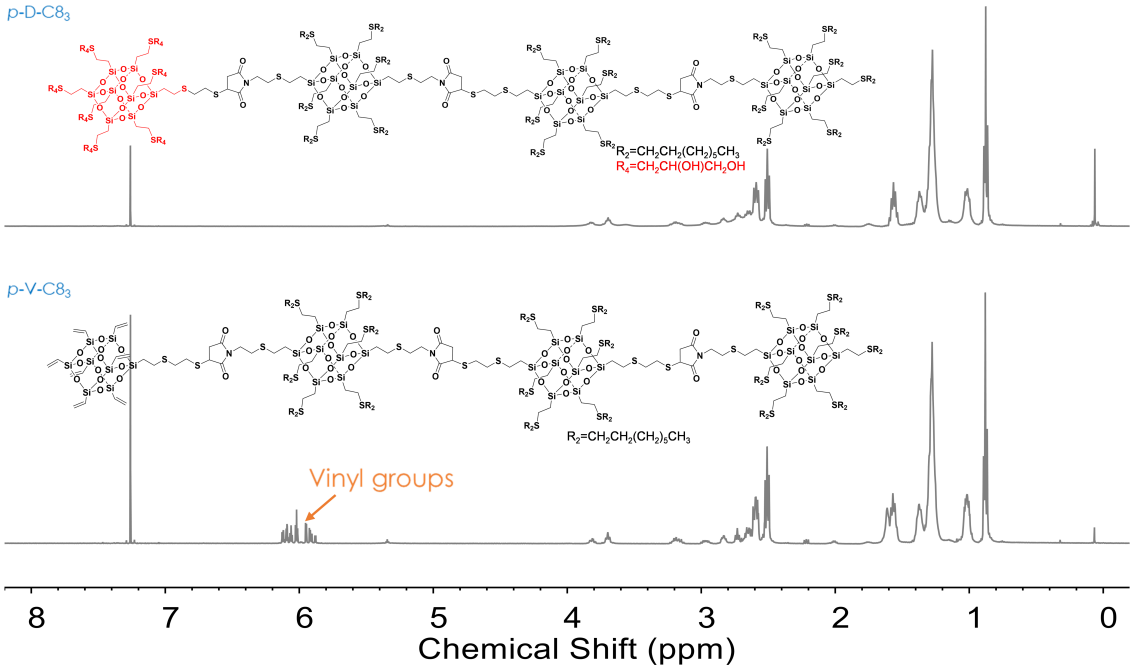


Figure S10. ^{1}H NMR spectra of *para*-V-C8$_3$ and *para*-D-C8$_3$. Asterisks denote signals from $CDCl_3$.

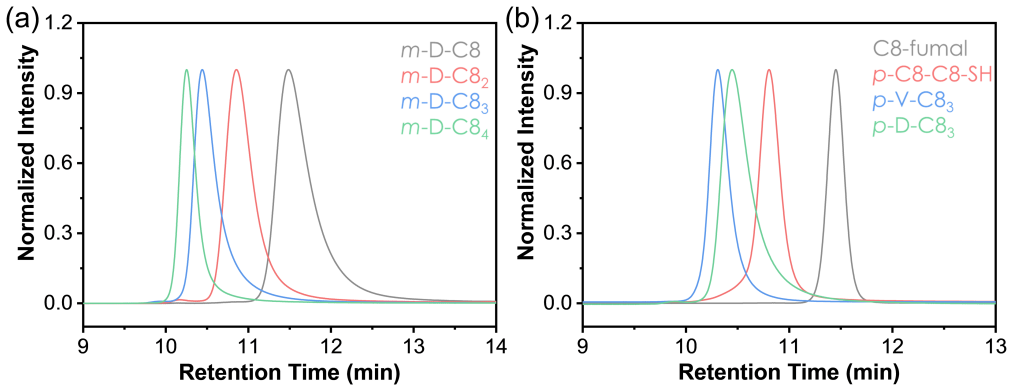


Figure S11. SEC traces of amphiphilic POSS chains: *meta*-D-C8$_n$ (a) and *para*-D-C8$_3$ (b).

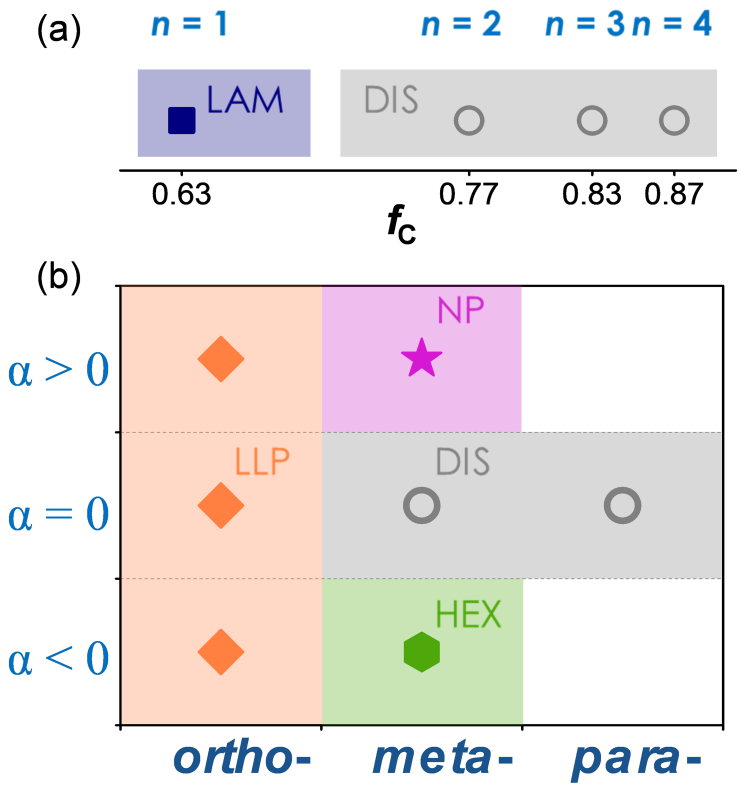


Figure S12. Phase portrait of amphiphilic giant molecules *meta*-D-C8$_n$ (a), and giant molecules with different regio-configuration or molecular geometry (b).

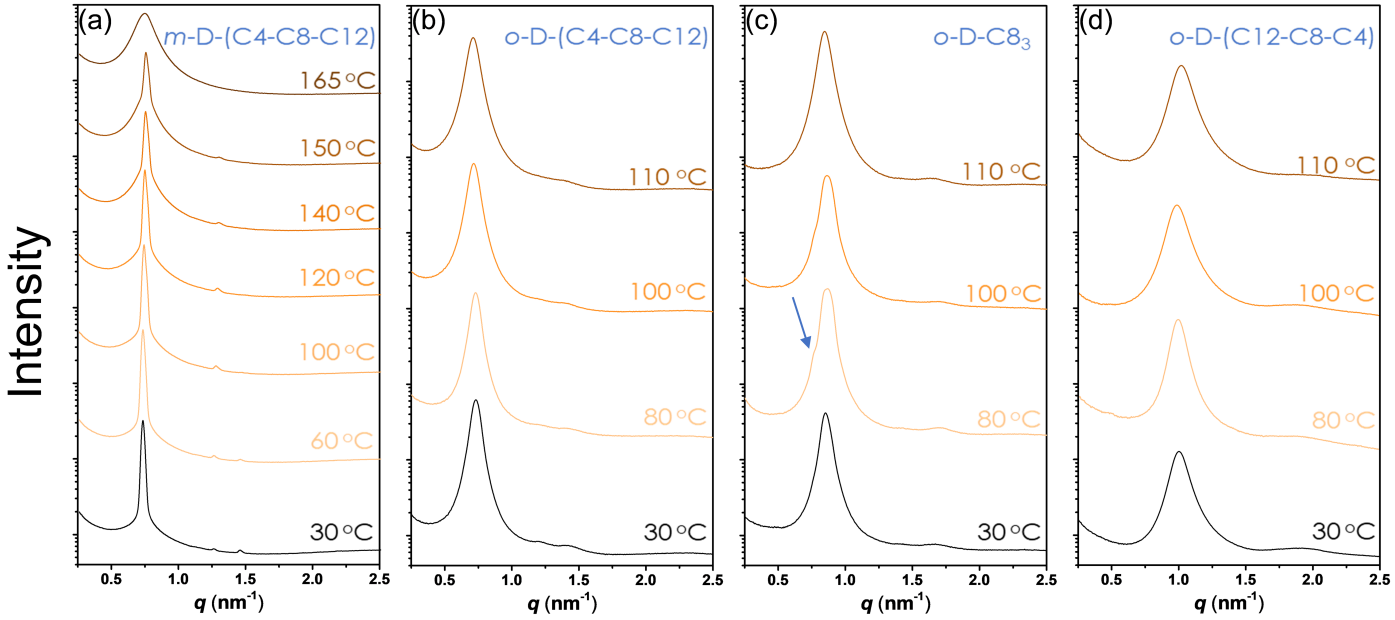


Figure S13. Temperature-dependent SAXS profiles of *meta*-D-(C4-C8-C12) (a), *ortho*-D-(C4-C8-C12) (b), *ortho*-D-C8$_3$ (c), and *ortho*-D-(C12-C8-C4) (d) (heating rate 10 °C/min). Data are shifted vertically for clarity.

6. References

(1) Liu, Z.; Chen, X.; Yang, Z.; Wang, S.; Gan, Z.; Li, G.; Dong, X.-H. Precise Amphiphilic Giant Polymeric Chain

Based on Nanosized Monomers with Exact Regio-Configuration. *ACS Nano* **2021**, *15* (7), 12367–12374. https://doi.org/10.1021/acsnano.1c04486.