Discrete Giant Polymeric Chains based on Nanosized Monomers

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1. Materials

The following chemicals were used as received: octavinylPOSS (Hybrid Plastics), 3-mercaptop-1-propanol (Sigma, 95%), 1-butanethiol (Sigma, 93%), 2,2,2-trifluoroethanethiol (Sigma, 95%), benzyl mercaptan (Sigma, 97%), 1-thioglycerol (Sigma, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 98%, TCI America), maleimide (Sigma, 95%), diisopropyl azodicarboxylate (DIAD, 97%, TCI America), dimethylchlorosilane (Sigma, 98%), hexamethylcyclotrisiloxane (Sigma, 97%), dimethylphenylsilane (TCI, 97%), Pd/C (Sigma, 10% loading), tris(pentafluorophenyl)borane (B(C₆F₅)₃, 98%, TCI America), triphenylphosphine (PPh₃, 97%, TCI America), tetrabromomethane (CBr₄, 98%, TCI America), potassium thioacetate (KSAc, 98%, TCI America), furan (Sigma, 98%), acetyl chloride (98%, TCI America), anhydrous sodium sulfate (Na₂SO₄, Sigma, 93%), tetrahydrofuran (THF), triethylamine (TEA), anhydrous pyridine, dioxane, 1 M phosphate buffer (pH = 7), toluene, petroleum ether (PE), ethyl acetate (EA), methanol (MeOH), chloroform (CHCl₃), dichloromethane (CH₂Cl₂). Azodiisobutyronitrile (AIBN, 98%, TCI America) was re-crystallized from methanol three times before used. Anhydrous solvents, including toluene, dichloromethane, N,N'-dimethylformamide (DMF), were obtained with an INERT Pure Solv System (Inert Corporation, USA).

2. Characterizations

**Nuclear Magnetic Resonance (NMR).** All ¹H NMR spectra were acquired in CDCl₃ using a Bruker 400 MHz NMR spectrometer. The spectra were referenced to the residual solvent peak in CDCl₃ at δ 7.27 ppm. ²⁹Si NMR spectra were acquired in CDCl₃ using a Bruker 99 MHz NMR spectrometer and referenced to tetramethylsilane (TMS) at δ 0.00 ppm.

**Size exclusion chromatography (SEC).** SEC analyses were measured at 40 °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, using THF as eluent. The flow-rate was 0.6 mL/min.
Data acquisition was performed using EcoSEC software, and molecular weights and molecular weight distributions were calibrated with polystyrene standards (Polymer Laboratories).

**Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF).** MALDI-ToF mass spectroscopy (MS) were acquired 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, Sigma-Aldrich, >98%) was used as the matrix and prepared in CHCl₃ at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in CHCl₃ at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-ToF mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and maximize the sensitivity.

**Thermogravimetric Analysis (TGA).** Nonisothermal decomposition experiments were carried out on a thermogravimetric analysis instrument (Model Q500, TA Instruments) under nitrogen atmosphere protection. For each run, initial mass of the samples was about 3 mg. The samples were scanned from 30 to 500°C with a heating rate of 10 °C/min.

**Differential Scanning Calorimetry (DSC).** Thermal transitions of all the samples were characterized utilizing a PerkinElmer PYRIS Diamond DSC with an Intracooler 2P apparatus. The samples were sealed in a DSC pan with an initial mass of about 5-8 mg and scanned from -60 to 80 °C with a heating/cooling rate of 5 °C/min under nitrogen flow.
3. Syntheses

3.1 POSS Monomers with Diverse Surface Functionalities

Scheme S1. Synthetic route of the POSS based monomers with diverse functionalities: (i) RSH, DMPA, THF, 25 °C, 365 nm × 30 min; (ii) Furan protected maleimide, DIAD, PPh₃, THF, 0 °C, 12 h; (iii) CBr₄, PPh₃, CH₂Cl₂, 0 °C, 2 h; (iv) potassium thioacetate, KI, THF/MeOH, 75 °C, 12 h.

3.1.1 Furan-protected maleimide. To a 250 mL round-bottom flask were added with maleimide (9.7 g, 0.1 mol) and furan (13.6 g, 0.2 mol). The mixture was dissolved in 160 mL of toluene. The flask was sealed and heated at 90 °C for 12 h. After cooling to room temperature, the product precipitated out as a white solid. The mixture was filtered and the filter cake was washed with 3×150 mL cold toluene. The product was dried under vacuum at 25 °C overnight to afford furan-protected maleimide as a white crystal (14.7 g, yield: 89%).

¹H NMR (400 MHz, CDCl₃, ppm, δ): 8.20 (s, 1H, -NH-), 6.53 (s, 2H, -CH=CH-), 5.32 (t, J = 0.8 Hz, 2H, -CH(O)-C-), 2.90 (s, 2H, -CH(-C=O)-CH-).

3.1.2 para-, meta-, ortho-V₆POSS(OH)₂. Octaviny1POSS (30.0 g, 47.4 mmol), 3-mercapto-1-propanol (8.72 g, 94.8 mmol), and DMPA (140 mg, 0.55 mmol) were dissolved in 350 mL of THF, and irradiated with UV (365 nm) for 30 min. After removing solvent, the regio-isomers were isolated by silica gel chromatography. A gradient mixture of EA/DCM (v/v from 1/20 to 1/4) was used as eluents to afford the products as white
p-\text{VePOSS(OH)}_2 (1.2 g, yield: 3.1\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 6.15-5.87 (m, 18H, -CH=CH\textsubscript{2}), 3.76 (t, \(J = 6.0\) Hz, 4H, -CH\textsubscript{2}OH), 2.69-2.65 (m, 8H, -CH\textsubscript{2}CH\textsubscript{2}SCH\textsubscript{2}CH\textsubscript{2}-), 1.85 (tt, \(J = 7.1, 6.0\) Hz, 4H, -SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH), 1.07 (m, 4H, -SiCH\textsubscript{2}-). \textsuperscript{13}C NMR (77 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 137.14, 128.65, 61.77, 31.77, 28.44, 25.94, 13.04. \textsuperscript{29}Si NMR (99 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): -68.53, -80.35.

m-\text{VePOSS(OH)}_2 (2.8 g, yield: 7.2\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 6.15-5.86 (m, 18H, -CH=CH\textsubscript{2}), 3.76 (t, \(J = 6.1\) Hz, 4H, -CH\textsubscript{2}OH), 2.69-2.66 (m, 8H, -CH\textsubscript{2}CH\textsubscript{2}SCH\textsubscript{2}CH\textsubscript{2}-), 1.84 (tt, \(J = 7.0, 6.0\) Hz, 4H, -SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH), 1.07 (m, 4H, -SiCH\textsubscript{2}-). \textsuperscript{29}Si NMR (99 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): -68.52, -80.23, -80.35, -80.48.

o-\text{VePOSS(OH)}_2 (3.5 g, yield: 9.1\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 6.14-5.87 (m, 18H, -CH=CH\textsubscript{2}), 3.76 (t, \(J = 6.0\) Hz, 4H, -CH\textsubscript{2}OH), 2.69-2.64 (m, 8H, -CH\textsubscript{2}CH\textsubscript{2}SCH\textsubscript{2}CH\textsubscript{2}-), 1.85 (tt, \(J = 7.0, 6.1\) Hz, 4H, -SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH), 1.08 (m, 4H, -SiCH\textsubscript{2}-). \textsuperscript{29}Si NMR (99 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): -68.63, -80.22, -80.36.

3.1.3 \(p\)-\text{R\textsubscript{6}POSS(OH)}\textsubscript{2}, \(p\)-\text{VePOSS(OH)}\textsubscript{2} (1.36 g, 1.66 mmol), R-SH (14.9 mmol, corresponding to 1.37 g of 1-butanol, 1.49 g of 2,2,2-trifluoroethanol, or 1.85 g of benzyl mercaptan), and DMPA (41.0 mg, 0.16 mmol) were dissolved in 13 mL of THF. After UV irradiation (365 nm) for 30 min, solvent was removed, and the residue was purified by silica gel chromatography with PE/EA (4/1, v/v) as eluent to afford the products (colorless oil liquids). 

\(p\)-\text{C\textsubscript{6}POSS(OH)}\textsubscript{2} (1.68 g, yield: 74.6\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 3.76 (q, \(J = 5.8\) Hz, 4H, HOCH\textsubscript{2}CH\textsubscript{2}-), 2.50-2.67 (m, 32H, -CH\textsubscript{2}SCH\textsubscript{2}-), 1.86 (h, \(J = 7.0\) Hz, 4H, -SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH), 1.56 (m, 12H, -SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.43 (h, \(J = 7.3\) Hz, 12H, -SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.05 (m, 16H, -SiCH\textsubscript{2}-), 0.94 (m, 18H, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (77 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 61.58, 31.98, 31.57, 28.46, 25.92, 22.04, 13.72, 13.01, 12.88.
**Supporting Information**

$p$-F₆POSS(OH)₂ (1.97 g, yield: 78.4%). $^1$H NMR (400 MHz, CDCl₃, ppm, δ): 3.77 (q, J = 5.2 Hz, 4H, HOCH₂CH₂-), 3.12 (q, J = 9.9 Hz, 12H, -SCH₂CF₃), 2.46-2.68 (m, 20H, -CH₂SCH₂CF₃, -CH₂SCH₂CH₂-), 1.85 (p, J = 6.6 Hz, 4H, -SCH₂CH₂CH₂OH), 1.05 (m, 16H, -SiCH₂-).

$p$-P₆POSS(OH)₂ (2.21 g, yield: 85.3%). $^1$H NMR (400 MHz, CDCl₃, ppm, δ): 7.23-7.35 (m, 30H, -SCH₂Ph), 3.74 (q, J = 4.9 Hz, 4H, HOCH₂CH₂-), 3.70 (m, 14H, -SCH₂Ph), 2.41-2.65 (m, 20H, -CH₂SCH₂Ph, -CH₂SCH₂CH₂-), 1.84 (p, J = 6.0 Hz, 4H, -SCH₂CH₂CH₂OH), 1.01 (m, 16H, -SiCH₂-).

3.1.4 Furan-protected Maleimide-RPOSS ($p$-Fu-Mal-R₆POSSOH). $p$-R₆POSS(OH)₂ (2.0 mmol, corresponding to 2.72 g of C₆POSS(OH)₂, 3.03 g of F₆POSS(OH)₂, or 3.13 g of P₆POSS(OH)₂), furan-protected maleimide (0.33 g, 2.0 mmol), and triphenylphosphine (PPh₃, 0.79 g, 3.0 mmol) were added to a round-bottom flask with anhydrous THF (25 mL), purged with nitrogen. The reaction mixture was stirred and cooled to 0 °C in an ice bath and diisopropyl azodicarboxylate (DIAD, 0.61 g, 3.0 mmol) was added dropwise. The solution was allowed to stir for 8 h at room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with PE/EA (3/1, v/v) as eluent to afford Fu-Mal-R₆POSSOH.

$p$-Fu-Mal-C₆POSSOH (1.76 g, yield: 58.6%). $^1$H NMR (400 MHz, CDCl₃, ppm, δ): 6.52 (d, J = 0.9 Hz, 2H, -CH=CH-), 5.26 (d, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.75 (t, J = 6.1 Hz, 2H, HOCH₂CH₂-), 3.58 (t, J = 7.1 Hz, 2H, -NCH₂CH₂-), 2.85 (s, 2H, -CH(-C=O)CH-), 2.52-2.65 (m, 32H, -CH₂SCH₂-), 1.84 (m, 4H, -CH₂CH₂CH₂-), 1.57 (m, 12H, -CH₂CH₂CH₃), 1.42 (dq, J = 14.6, 7.3 Hz, 12H, -CH₂CH₃CH₃), 1.02 (m, 16H, -SiCH₂CH₂-), 0.93 (m, 18H, -CH₂CH₂CH₃). $^{13}$C NMR (77 MHz, CDCl₃, ppm, δ): 176.07, 136.38, 80.82, 61.35, 47.32, 37.83, 31.91, 31.38, 28.05, 28.29, 27.10, 25.77, 21.91, 13.62, 12.86, 12.79.

$p$-Fu-Mal-F₆POSSOH (1.71 g, yield: 51.6%). $^1$H NMR (400 MHz, CDCl₃, ppm, δ): 6.52 (d, J = 1.0 Hz, 2H, -CH=CH-), 5.24 (d, J = 0.9 Hz, 2H, -CH(-O-)C-), 3.78 (t, J = 6.0 Hz, 2H, HOCH₂CH₂-), 3.59 (t, J = 5.6 Hz, -CH=CH-), 5.24 (d, J = 0.9 Hz, 2H, -CH=CH-), 5.24 (d, J = 0.9 Hz, 2H, -CH(-O-)C-), 3.78 (t, J = 6.0 Hz, 2H, HOCH₂CH₂-), 3.59 (t, J = 5.6 Hz, -CH=CH-), 5.24 (d, J = 0.9 Hz, 2H, -CH=CH-), 5.24 (d, J = 0.9 Hz, 2H, -CH(-O-)C-), 3.78 (t, J = 6.0 Hz, 2H, HOCH₂CH₂-), 3.59 (t, J = 5.6 Hz,
2H, -NCH₂CH₂-), 3.09 (m, 12H, -SCH₂CF₃), 2.85 (s, 2H, -CH(-C=O)CH⁻), 2.52-2.80 (m, 20H, -CH₂SCH₂CF₃, -CH₂SCH₂CH₂-), 1.85 (m, 4H, -CH₂CH₂CH₂-), 1.05 (m, 16H, -SiCH₂CH₂-).

**p-Fu-Mal-P₆POSSOH** (1.88 g, yield: 54.9%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 7.22-7.34 (m, 30H, -SCH₂Ph), 6.48 (d, J = 1.0 Hz, 2H, -CH=CH⁻), 5.25 (t, J = 0.8 Hz, 2H, -CH(-O-)-C⁻), 3.75-3.70 (m, 14H, HOCH₂CH₂-, -SCH₂Ph), 3.58 (t, J = 7.0 Hz, 2H, -NCH₂CH₂-), 2.82 (s, 2H, -CH(-C=O)CH⁻), 2.40-2.64 (m, 20H, -CH₂SCH₂Ph -CH₂SCH₂CH₂-), 1.85 (m, 4H, -CH₂CH₂CH₂-), 1.01 (m, 16H, -SiCH₂CH₂-).

### 3.1.5 **p-RPOSS monomer**

**p-Fu-Mal-R₆POSSOH** (1.0 mmol, corresponding to 1.51 g of **p-Fu-Mal-C₆POSSOH**, 1.66 g of **p-Fu-Mal-F₆POSSOH**, or 1.71 g of **p-Fu-Mal-P₆POSSOH**) was dissolved in 15 mL of anhydrous CH₂Cl₂ in a 25 mL round-bottom flask. CBr₄ (0.66 g, 2.0 mmol) was then added, and the mixture was transferred into an ice bath. When completely dissolved, PPh₃ (0.52 g, 2.0 mmol) was slowly added and the ice bath was removed. After stirring for 4 hours, MeOH (20 mL), KI (20 mg), and potassium thioacetate (0.23 g, 2.0 mmol) were added, and the mixture was further stirred at 75 °C for 12 h under argon atmosphere. The solvent was then removed under vacuum and the crude product was purified by silica gel column chromatography with PE/EA (5/1, v/v) as eluent to afford monomers.

**p-CPOSS monomer** (1.32 g, yield: 84.3%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 6.51 (d, J = 1.0 Hz, 2H, -CH=CH⁻), 5.26 (t, J = 0.8 Hz, 2H, -CH(-O-)-C⁻), 3.58 (t, J = 7.1 Hz, 2H, -NCH₂CH₂-), 2.96 (t, J = 7.2 Hz, 2H, -(O=C)SCH₂CH₂-), 2.85 (s, 2H, -CH(-C=O)CH⁻), 2.48-2.61 (m, 32H, -CH₂SCH₂-), 2.33 (t, J = 7.4 Hz, 3H, CH₃(O=O)-SCH₂CH₂-), 1.84 (td, J = 7.2, 5.4 Hz, 4H, -CH₂CH₂CH₂S-), 1.55 (pd, J = 7.9, 7.5, 2.5 Hz, 12H, -CH₂CH₂CH₃), 1.40 (hd, J = 7.3, 1.6 Hz, 12H, -CH₂CH₂CH₃), 1.01 (m, 16H, -SiCH₂CH₂-), 0.92 (m, 18H, -CH₂CH₂CH₃). ¹³C NMR (77 MHz, CDCl₃, ppm, δ): 195.30, 176.03, 136.39, 80.83, 47.33, 37.85, 31.46, 31.39, 30.54, 30.42, 29.07, 28.51, 27.90, 27.12, 25.78, 25.73, 25.55, 21.92, 13.64, 12.91, 12.87, 12.83, 12.72.

**p-FPOSS monomer** (1.45 g, yield: 84.3%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 6.52 (d, J = 1.0 Hz, 2H, -
CH=CH-), 5.26 (t, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.59 (t, J = 7.1 Hz, 2H, -NCH$_2$CH$_2$-), 3.11 (m, 12H, -SCH$_2$CF$_3$), 2.97 (t, J = 7.2 Hz, 2H, CH$_3$(O=C)SCH$_2$CH$_2$-), 2.85 (s, 2H, -CH(-C=O)CH_), 2.52-2.77 (m, 20H, -CH$_2$SCH$_2$CF$_3$, -CH$_2$SCH$_2$CH$_2$-), 2.34 (t, J = 7.4 Hz, 3H, CH$_3$(O=C)SCH$_2$CH$_2$-), 1.85 (td, J = 7.3, 3.5 Hz, 4H, -CH$_2$CH$_2$CH$_2$S-), 1.05 (m, 16H, -SiCH$_2$CH$_2$-).

$^{13}$C NMR (77 MHz, CDCl$_3$, ppm, δ): 195.99, 176.22, 136.47, 129.30, 127.10, 124.89, 122.71, 80.93, 47.38, 37.92, 30.57, 30.54, 29.17, 28.68, 27.92, 27.18, 25.61, 25.57, 25.42, 12.60, 12.48, 12.26.

$p$-PPOSS monomer (1.46 g, yield: 82.5%). $^1$H NMR (400 MHz, CDCl$_3$, ppm, δ): 7.23-7.34 (m, 30H, -SCH$_2$Ph), 6.48 (d, J = 1.0 Hz, 2H, -CH=CH-), 5.25 (t, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.70 (d, J = 5.1 Hz, 12H, -SCH$_2$Ph), 3.59 (t, J = 7.1 Hz, 2H, -NCH$_2$CH$_2$-), 2.97 (t, J = 7.2 Hz, 2H, CH$_3$(O=C)SCH$_2$CH$_2$-), 2.82 (s, 2H, -CH(-C=O)CH_), 2.41-2.58 (m, 20H, -CH$_2$SCH$_2$Ph, -CH$_2$SCH$_2$CH$_2$-), 2.33 (s, 3H, CH$_3$(O=C)-SCH$_2$CH$_2$-), 1.84 (td, J = 7.3, 3.3 Hz, 4H, -CH$_2$CH$_2$CH$_2$S-), 1.04 (m, 16H, -SiCH$_2$CH$_2$-). $^{13}$C NMR (77 MHz, CDCl$_3$, ppm, δ): 195.36, 176.05, 138.21, 136.34, 128.65, 128.39, 126.88, 80.79, 47.28, 37.86, 35.78, 30.55, 30.41, 29.07, 25.52, 27.91, 27.13, 25.67, 25.49, 24.98, 24.94, 12.73, 12.62, 12.42.

3.2 Discrete Homo Polymeric Chains

Each IEG cycle consists of two steps of deprotection (Mal-R$_n$ and R$_m$-SH) and one coupling reaction (R$_{n+m}$).

![Scheme S2](image)

**Scheme S2.** Iterative exponential growth of discrete POSS chains: (i) Acetyl chloride, -78 °C, CH$_2$Cl$_2$/MeOH, 7h; (ii) Toluene, 110 °C, 5 h; (iii) TEA, CHCl$_3$, 25 °C, 8 h.
3.2.1 Dimer: \( p-R_2 \)

\( p\text{-Mal-R}_1 \): monomer (1.0 mmol, corresponding to 1.56 g of \( p\text{-C}_1 \), 1.72 g of \( p\text{-F}_1 \), or 1.77 g of \( p\text{-P}_1 \)) was dissolved in 30 mL of toluene in a 100 mL three-neck flask equipped with a condenser. After stirring and refluxing at 120 °C under argon flow for about 6 h, TLC indicated the reaction was complete. Toluene was removed under vacuum. The residue was dried under vacuum at 25 °C for 24 h to afford \( p\text{-Mal-R}_1 \) as colorless oil (\( p\text{-Mal-C}_1 \): 1.47 g, yield: 98%; \( p\text{-Mal-F}_1 \): 1.60 g, yield: 97%; \( p\text{-Mal-P}_1 \): 1.67 g, yield: 98%).

\( p\text{-R}_1\text{-SH} \): monomer (1.0 mmol, corresponding to 1.56 g of \( p\text{-C}_1 \), 1.72 g of \( p\text{-F}_1 \), or 1.77 g of \( p\text{-P}_1 \)) was dissolved in 10 mL of MeOH and 30 mL of CH$_2$Cl$_2$ in a 100 mL two-neck round-bottom flask. The mixture was cooled to -78 °C. Acetyl chloride (15.0 mL, 0.11 mol) was then added dropwise to the solution. The mixture was warmed to room temperature and further stirred for 12 h. The reaction mixture was quenched with 20 mL water and washed with 30 mL saturated NaHCO$_3$ (aq.). The organic layer was combined and washed with 30 mL of water and dried with anhydrous Na$_2$SO$_4$. DCM was removed under vacuum to afford \( p\text{-R}_1\text{-SH} \) as colorless oil liquid (\( p\text{-C}_1\text{-SH} \): 1.43 g, yield: 94%; \( p\text{-F}_1\text{-SH} \): 1.53 g, yield: 91%; \( p\text{-P}_1\text{-SH} \): 1.60 g, yield: 93%).

\( p\text{-R}_2 \): \( p\text{-Mal-R}_1 \): (\( p\text{-Mal-C}_1 \): 1.47 g; \( p\text{-Mal-F}_1 \): 1.60 g; \( p\text{-Mal-P}_1 \): 1.67 g) and mer-SH (\( p\text{-C}_1\text{-SH} \): 1.43 g; \( p\text{-F}_1\text{-SH} \): 1.53 g; \( p\text{-P}_1\text{-SH} \): 1.60 g) were dissolved in 25 mL of anhydrous CHCl$_3$ in a 50 mL two-neck round-bottom flask equipped with a 25 mL slow-addition apparatus under argon atmosphere at 25 °C. TEA (1.0 mL, 7.3 mmol) was added dropwise to the solution and the mixture was stirred for 24 h. The reaction mixture was quenched with 20 mL of water and washed with 30 mL of saturated NaHCO$_3$ (aq.). The combined organic layer was dried with anhydrous Na$_2$SO$_4$ and the solvent was removed to afford the crude product, which was further purified by column chromatography with PE/EA (4/1) as eluent to give the \( p\text{-R}_2 \) as colorless oil liquid. \( p\text{-C}_2 \) (2.00 g, yield: 69%). $^1$H NMR (400 MHz, CDCl$_3$, ppm, $\delta$): 6.51 (s, 2H, -CH=CH-), 5.26 (t, $J = 1.0$ Hz, ...)
2H, -CH(-O-)C-, 3.73 (dd, J = 9.0, 3.7 Hz, 1H, -SCH(C=O)CH2-), 3.59 (m, 4H, -NCH2CH2-), 3.14, 3.05 (m, 2H, -CHCH2(C=O)-), 2.97 (s, 2H, CH3(O=C)SCH2CH2-), 2.85 (t, J = 5.5 Hz, 2H, -CH(-C=O)CH-), 2.47-2.63 (m, 66H, -CH2SCH2-, -CH2SCH-), 2.34 (s, 3H, CH3(O=C-)SCH2CH2-), 1.86 (m, 8H, -CH2CH2CH2S-), 1.56 (m, 24H, -CH2CH2CH3), 1.42 (m, 24H, -CH2CH2CH3), 1.02 (m, 32H, -SiCH2CH2-), 0.93 (t, J = 7.3 Hz, 36H, -CH2CH2CH3). 13C NMR (77 MHz, CDCl3, ppm, δ): 194.93, 175.81, 174.20, 136.20, 80.65, 47.15, 38.65, 37.83, 37.63, 35.73, 31.27, 31.17, 30.36, 30.33, 30.20, 30.12, 28.90, 28.56, 28.27, 27.70, 26.93, 26.80, 25.56, 25.49, 25.29, 21.73, 13.47, 12.68, 12.53.

p-F2 (1.95 g, yield: 63%). 1H NMR (400 MHz, CDCl3, ppm, δ): 6.52 (s, 2H, -CH=CH-), 5.26 (t, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.75 (d, J = 5.6 Hz, 1H, -SCH(C=O)CH2-), 3.59 (dt, J = 14.2, 7.1 Hz, 4H, -NCH2CH2-), 3.04-3.10 (m, 26H, -SCH2CF3, -CHCH2(C=O)-), 2.97 (t, J = 5.1 Hz, 2H, CH3(O=C)SCH2CH2-), 2.85 (s, 2H, -CH(-C=O)CH-), 2.50-2.77 (m, 42H, -CH2SCH2CF3, -CH2SCH2CH2-, -CH2SCH-), 2.34 (s, 3H, CH3(O=C-)SC-), 1.86 (m, 8H, -CH2CH2CH2S-), 1.05 (ddt, J = 10.8, 8.0, 3.9 Hz, 32H, -SiCH2CH2-).

p-P2 (2.16 g, yield: 66%). 1H NMR (400 MHz, CDCl3, ppm, δ): 7.25-7.34 (m, 60H, -SCH2Ph), 6.48 (s, 2H, -CH=CH-), 5.24 (t, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.70-3.74 (m, 25H, -SCH2Ph, -SCH(C=O)CH2-), 3.58 (q, J = 7.9, 7.4 Hz, 4H, -NCH2CH2-), 3.1, 3.14 (m, 2H, -CHCH2(C=O)-), 2.97 (t, J = 5.3 Hz, 2H, CH3(O=C)SCH2CH2-), 2.81 (m, 2H, -CH(-C=O)CH-), 2.41-2.63 (m, 42H, -CH2SCH2Ph, -CH2SCH2CH2-, -CH2SCH-), 2.32 (s, 3H, CH3(O=C-)SCH2CH2-), 1.85 (m, 8H, -CH2CH2CH2S-), 0.96 (q, J = 9.3 Hz, 32H, -SiCH2CH2-).

3.2.2 4mer: p-R4

p-Mal-R2: p-R2 (0.3 mmol, p-C2: 0.91 g; p-F2: 1.00 g; p-P2: 1.03 g) was dissolved in 20 mL of toluene in a 50 mL three-neck flask equipped with a condenser. The mixture was stirred and refluxed at 120 °C under argon flow for about 6 h. TLC showed the reaction was complete. After cooling to room temperature, toluene was
evaporated under vacuum. The residue was dried under vacuum at 25 °C for 24 h to afford p-Mal-R\textsubscript{2} as colorless oil liquids (p-Mal-C\textsubscript{2}: 0.81 g, yield: 92%; p-Mal-F\textsubscript{2}: 0.90 g, yield: 91%; p-Mal-P\textsubscript{2}: 0.95 g, yield: 94%).

\textit{p-R\textsubscript{2}-SH}: p-R\textsubscript{2} (0.3 mmol, p-C\textsubscript{2}: 0.91 g; p-F\textsubscript{2}: 1.00 g; p-P\textsubscript{2}: 1.03 g) was dissolved in 6 mL of MeOH and 15 mL of CH\textsubscript{2}Cl\textsubscript{2} in a 50 mL two-neck round-bottom flask. The mixture was cooled to -78 °C. Acetyl chloride (8.0 mL, 59 mmol) was then added dropwise to the solution. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with 20 mL of water and washed with 30 mL of saturated NaHCO\textsubscript{3} (aq.). The organic layer was combined and washed with 30 mL of water and dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}. DCM was removed under vacuum to afford p-R\textsubscript{2}-SH as colorless oil liquid (p-C\textsubscript{2}-SH: 0.79 g, yield: 89%; p-F\textsubscript{2}-SH: 0.87 g, yield: 88%; p-P\textsubscript{2}-SH: 0.90 g, yield: 90%).

\textit{p-R\textsubscript{4}:} p-Mal-R\textsubscript{2} (p-Mal-C\textsubscript{2}: 0.81 g; p-Mal-F\textsubscript{2}: 0.90 g; p-Mal-P\textsubscript{2}: 0.95 g) and p-R\textsubscript{2}-SH (p-C\textsubscript{2}-SH: 0.79 g; p-F\textsubscript{2}-SH: 0.87 g; p-P\textsubscript{2}-SH: 0.90 g) were dissolved in 20 mL of anhydrous CHCl\textsubscript{3} in a 50 mL two-neck round-bottom flask equipped with a 25 mL slow-addition apparatus under argon atmosphere at 25 °C. TEA (0.8 mL, 5.8 mmol) was added dropwise to the solution and the mixture was stirred for about 24 h. The reaction mixture was washed with 30 mL of saturated NaHCO\textsubscript{3} (aq.). The combined organic layer was dried with anhydrous Na\textsubscript{2}SO\textsubscript{4} and the solvent was evaporated to afford the crude product, which was purified by recycling preparative SEC to give the p-R\textsubscript{4} as colorless oil liquid.

\textit{p-C\textsubscript{4}} (0.88 g, yield: 55%). \textit{H} NMR (400 MHz, CDCl\textsubscript{3}, ppm, δ): 6.52 (s, 2H, -CH=CH\textsubscript{-}), 5.26 (t, \textit{J} = 1.0 Hz, 2H, -CH(-O-)C\textsubscript{-}), 3.74 (dd, \textit{J} = 9.0, 3.6 Hz, 3H, -SCH(C=O)CH\textsubscript{2}-), 3.58 (dt, \textit{J} = 13.6, 7.2 Hz, 8H, -NCH\textsubscript{2}CH\textsubscript{2}-), 3.14, 3.05 (m, 6H, -CHCH\textsubscript{2}(C=O)-), 2.97 (t, \textit{J} = 7.2 Hz, 2H, CH\textsubscript{3}(O=C)SCH\textsubscript{2}CH\textsubscript{2}-), 2.84 (s, 2H, -CH(-C=O)CH\textsubscript{-}), 2.44-2.63 (m, 134H, -CH\textsubscript{2}SCH\textsubscript{2}, -CH\textsubscript{2}SCH\textsubscript{-}), 2.36 (s, 3H, CH\textsubscript{3}(O=C-)SCH\textsubscript{2}CH\textsubscript{2}-), 1.85 (m, 16H, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}S\textsubscript{-}), 1.57 (m, 48H, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.42 (m, 48H, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.03 (m, 64H, -SiCH\textsubscript{2}CH\textsubscript{2}-),...
0.94 (t, J = 7.9 Hz, 72H, -CH₂CH₂CH₃).

**p-F₄** (1.04 g, yield: 59%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 6.52 (s, 2H, -CH=CH-), 5.26 (t, J = 1.0 Hz, 2H, -CH(=O)C-), 3.73 (dd, J = 9.1, 3.6 Hz, 3H, -SCH(C=O)CH₂-), 3.53 (dt, J = 13.7, 7.1 Hz, 8H, -NCH₂CH₂-), 3.04-3.10 (m, 54H, -SCH₂CF₃, -CHCH₂(C=O)-), 2.97 (t, J = 7.6 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.86 (s, 2H, -CH(-C=O)CH-), 2.50-2.77 (m, 86H, -CH₂SCH₂CF₃, -CH₂SCH₂CH₂-, -CH₂SCH-), 2.37 (s, 3H, CH₃(O=C)-SC-), 1.82 (m, 16H, -CH₂CH₂CH₂S-), 1.05 (m, 64H, -SiCH₂CH₂-).

**p-P₄** (1.00 g, yield: 54%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 7.26-7.34 (m, 120H, -SCH₂Ph), 6.48 (s, 2H, -CH=CH-), 5.23 (t, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.70-3.75 (m, 51H, -SCH₂Ph, -SCH(C=O)CH₂-), 3.58 (dt, J = 13.1, 7.9 Hz, 8H, -NCH₂CH₂-), 3.11, 3.14 (m, 6H, -CHCH₂(C=O)-), 2.93 (t, J = 7.3 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.84 (s, 2H, -CH(-C=O)CH-), 2.41-2.63 (m, 86H, -CH₂SCH₂Ph, -CH₂SCH₂CH₂-, -CH₂SCH-), 2.33 (s, 3H, CH₃(O=C)-SCH₂CH₂-), 1.82 (m, 16H, -CH₂CH₂CH₂S-), 0.98 (m, 64H, -SiCH₂CH₂-).

### 3.2.3 8mer: **p-R₈**

**p-Mal-R₄**: **p-R₄** (0.07 mmol, **p-C₄**: 0.41 g; **p-P₄**: 0.47 g) was dissolved in 15 mL of toluene in a 50 mL three-neck flask equipped with a condenser. The mixture was stirred and refluxed at 120 ºC under argon flow for about 6 h. TLC showed the reaction was complete. After cooling to room temperature, toluene was evaporated under vacuum. The residue was dried under vacuum at 25 ºC for 24 h to afford **p-Mal-R₄** as colorless oil liquid (**p-Mal-C₄**: 0.37 g, yield: 90%; **p-Mal-P₄**: 0.39 g, yield: 89%).

**p-R₄-SH**: **p-R₄** (0.07 mmol, **p-C₄**: 0.41 g; **p-P₄**: 0.47 g) was dissolved in 6 mL of MeOH and 22 mL of CH₂Cl₂ in a 50 mL two-neck round-bottom flask equipped with a condenser. The mixture was cooled to -78 ºC. Acetyl chloride (8.0 mL, 59 mmol) was then added dropwise to the solution. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with 20 mL of water and washed with 30 mL of saturated NaHCO₃ (aq.). The organic layer was combined and washed with 30 mL of water and
dried with anhydrous Na₂SO₄. DCM was concentrated under vacuum to afford **p-R₄-SH** as colorless oil liquid (**p-C₄-SH**: 0.35 g, yield: 86%; **p-P₄-SH**: 0.38 g, yield: 88%).

**p-R₈**: **p-Mal-R₄** (**p-Mal-C₄**: 0.37 g; **p-Mal-P₄**: 0.39 g) and **p-R₄-SH** (**p-C₄-SH**: 0.35 g; **p-P₄-SH**: 0.38 g) were dissolved in 15 mL of anhydrous CHCl₃ in a 25 mL two-neck round-bottom flask equipped with a 5 mL slow-addition apparatus under argon atmosphere at 25 ºC. TEA (0.2 mL, 1.5 mmol) was added dropwise to the solution and the mixture was stirred for about 24 h. The reaction mixture was quenched with 20 mL water and washed with 30 mL saturated NaHCO₃ (aq.). The combined organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated to afford the crude product which was further purified by recycling preparative SEC to give the **p-R₈** as colorless oil liquid.

**p-C₈** (0.32 g, yield: 45%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 6.51 (s, 2H, -CH=CH-), 5.26 (t, J = 1.0 Hz, 2H, -CH₂(-O-)C-), 3.74 (dd, J = 9.5, 3.1 Hz, 7H, -SCH(C=O)CH₂-), 3.55 (dt, J = 13.1, 7.6 Hz, 16H, -NCH₂CH₂-), 3.14, 3.05 (m, 14H, -CHCH₂(C=O)-), 2.94 (t, J = 7.0 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.84 (s, 2H, -CH(-C=O)CH-), 2.47-2.63 (m, 270H, -CH₂SCH₂-, -CH₂SCH-), 2.34 (s, 3H, CH₃(O=C-)SCH₂CH₂-), 1.85 (m, 32H, -CH₂CH₂CH₂S-), 1.53 (m, 96H, -CH₂CH₂CH₃), 1.44 (m, 96H, -CH₂CH₂CH₃), 1.03 (m, 128H, -SiCH₂CH₂-), 0.94 (m, 144H, -CH₂CH₂CH₃).

**p-P₈** (0.42 g, yield: 54%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 7.25-7.34 (m, 240H, -SCH₂Ph), 6.48 (s, 2H, -CH=CH-), 5.25 (t, J = 1.0 Hz, 2H, -CH(-O-)C-), 3.71-3.74 (m, 103H, -SCH₂Ph, -SCH(C=O)CH₂-), 3.55 (dt, J = 13.1, 7.9 Hz, 16H, -NCH₂CH₂-), 3.11, 3.14 (m, 14H, -CHCH₂(C=O)-), 2.99 (t, J = 7.5 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.82 (s, 2H, -CH(-C=O)CH-), 2.41-2.63 (m, 174H, -CH₂SCH₂Ph, -CH₂SCH₂CH₂-), 2.33 (s, 3H, CH₃(O=C-)SCH₂CH₂-), 1.84 (m, 32H, -CH₂CH₂CH₂S-), 0.97 (m, 128H, -SiCH₂CH₂-).

### 3.2.4 16mer: **p-R₁₆**

**p-Mal-R₈**: **p-R₈** (8.5x10⁻³ mmol, **p-C₈**: 0.10 g) was dissolved in 80 mL of toluene in a 25 mL three-neck flask
equipped with a condenser. The mixture was stirred and refluxed at 120 °C under argon flow for about 6 h. TLC showed the reaction was complete. After cooling to room temperature, toluene was evaporated under vacuum. The residue was dried under vacuum at 25 °C for 24 h to afford \( p-\text{Mal-R}_8 \) as colorless oil liquid (\( p-\text{C}_8\text{-mal} \): 78 mg, yield: 78%).

\( p-\text{Rs-SH} \): \( p-\text{R}_8 \) (8.5\( \times 10^{-3} \) mmol, \( p-\text{C}_8 \): 0.10 g) was dissolved in 2 mL of MeOH and 8 mL of CH\(_2\)Cl\(_2\) in a 25 mL two-neck round-bottom flask equipped with a condenser. The mixture was cooled to -78 °C. Acetyl chloride (1.0 mL, 7 mmol) was then added dropwise to the solution. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with 20 mL of water and washed with 30 mL of saturated NaHCO\(_3\) (aq.). The organic layer was combined and washed with 30 mL of water and dried with anhydrous Na\(_2\)SO\(_4\). DCM was removed under vacuum to afford \( p-\text{Rs-SH} \) as colorless oil liquid (\( p-\text{C}_8\text{-SH} \): 71 mg, yield: 71%).

\( p-\text{R}_{16} \): \( p-\text{Mal-R}_8 \) (\( p-\text{Mal-C}_8 \): 78 mg) and \( p-\text{Rs-SH} \) (\( p-\text{C}_8\text{-SH} \): 71 mg) were dissolved in 10 mL of dry CHCl\(_3\) in a 25 mL two-neck round-bottom flask equipped with a 5 mL slow-addition apparatus under argon atmosphere at 25 °C. TEA (0.1 mL, 0.73 mmol) was added dropwise to the solution and the mixture was stirred for about 24 h. The reaction mixture was quenched with 20 mL of water and washed with 30 mL of 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 further purified by recycling preparative SEC to give the \( p-\text{R}_{16} \) as colorless oil liquid.

\( p-\text{C}_{16} \) (48 mg, yield: 32%). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm, \( \delta \)): 6.52 (s, 2H, -CH=CH\(_2\)), 5.26 (t, \( J = 1.0 \) Hz, 2H, -CH\(_2\)(O-)-C-), 3.74 (dd, \( J = 9.5, 3.1 \) Hz, 15H, -SCH(C=O)CH\(_2\)-), 3.55 (dt, \( J = 13.1, 7.6 \) Hz, 32H, -NCH\(_2\)CH\(_2\)-), 3.14, 3.05 (m, 30H, -CHCH\(_2\)(C=O)-), 2.95 (t, \( J = 7.1 \) Hz, 2H, CH\(_3\)(O=C)SCH\(_2\)CH\(_2\)-), 2.87 (s, 2H, -CH(-C=O)CH\(_2\)-), 2.47-2.63 (m, 542H, -CH\(_3\)SCH\(_2\)-, -CH\(_2\)SCH\(_2\)-), 2.35 (s, 3H, CH\(_3\)(O=C-)SCH\(_2\)CH\(_2\)-), 1.83
(m, 64H, -CH₂CH₂CH₂S-), 1.54 (m, 192H, -CH₂CH₃), 1.42 (m, 192H, -CH₂CH₃), 1.03 (m, 256H, -SiCH₂CH₂-), 0.94 (m, 288H, -CH₂CH₂CH₃).

3.3 Discrete Block Polymeric Chains

The deprotection and coupling reactions follow similar approach as described in section 3.2.

**Scheme S3.** Synthetic Route of Block Polymeric Chains: (i) TEA, CHCl₃, 25 °C, 8 h.

**p-C₄F₄** (560 mg, yield: 74%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 6.52 (s, 2H, -CH=CH-), 5.26 (t, J = 1.0 Hz, 2H, -CH(-O)-C-), 3.74 (dd, J = 9.1, 3.6 Hz, 1H, -SCH(C=O)CH₂-), 3.59 (dt, J = 13.1, 7.6 Hz, 4H, -NCH₂CH₂-), 3.06-3.19 (m, 14H, -SCH₂CF₃, -CHCH₂(C=O)-), 2.97 (t, J = 7.1 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.86 (s, 2H, -CH(-C=O)CH-), 2.48-2.77 (m, 54H, -CH₂SCH₂CF₃, -CH₂SCH₂-, -CH₂SCH₂-), 2.34 (s, 3H, CH₃(O=C)-SCH₂CH₂-), 1.84 (m, 8H, -CH₂CH₂CH₂S-), 1.58 (m, 12H, -CH₂CH₂CH₃), 1.41 (m, 12H, -CH₂CH₂CH₃), 1.03 (m, 32H, -SiCH₂CH₂-), 0.94 (t, J = 7.3 Hz, 18H, -CH₂CH₂CH₃).

**p-C₄F₄** (120 mg, yield: 51%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 6.52 (s, 2H, -CH=CH-), 5.26 (t, J = 1.0 Hz, 2H, -CH(-O)-C-), 3.75 (dd, J = 9.1, 3.6 Hz, 7H, -SCH(C=O)CH₂-), 3.58 (dt, J = 13.9, 7.0 Hz, 16H, -NCH₂CH₂-), 2.99-3.20 (m, 62H, -SCH₂CF₃, -CHCH₂(C=O)-), 2.92 (t, J = 7.3 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.85 (s, 2H, -CH(-C=O)CH-), 2.51-2.78 (m, 222H, -CH₂SCH₂CF₃, -CH₂SCH₂-, -CH₂SCH₂-), 2.35 (s, 3H, -CH₃), 2.14-2.19 (m, 180H, -SCH₂CH₂-), 2.09-2.13 (m, 180H, -CH₂SCH₂-), 2.03-2.07 (m, 180H, -CH₂SCH₂-), 1.01-1.05 (m, 32H, -SiCH₂CH₂-), 0.92 (t, J = 7.3 Hz, 18H, -CH₂CH₂CH₃).
$p$-C$_1$P$_1$ (760 mg, yield: 77%). $^1$H NMR (400 MHz, CDCl$_3$, ppm, δ): 7.25-7.34 (m, 30H, -SCH$_2$Ph), 6.52 (s, 2H, -CH=CH$_2$), 5.27 (t, $J = 1.0$ Hz, 2H, -CH(-O-)C-), 3.70-3.74 (m, 13H, -SCH$_2$Ph, -SCH(C=O)CH$_2$-), 3.59 (dt, $J = 14.1$, 7.4 Hz, 4H, -NCH$_2$CH$_2$-), 3.14, 3.05 (m, 2H, -CHCH$_2$(C=O)-), 2.95 (t, $J = 7.3$ Hz, 2H, CH$_3$(O=C)SCH$_2$CH$_2$-), 2.87 (s, 2H, -CH(-C=O)CH$_2$-), 2.47-2.63 (m, 54H, -CH$_2$SCH$_2$-, -CH$_2$SCH$_2$-), 2.35 (s, 3H, CH$_3$(O=C)-SCH$_2$CH$_2$-), 1.83 (m, 8H, -CH$_2$CH$_2$CH$_2$S-), 1.55 (m, 12H, -CH$_2$CH$_2$CH$_3$), 1.44 (m, 12H, -CH$_2$CH$_2$CH$_3$), 1.03 (m, 32H, -SiCH$_2$CH$_2$-), 0.94 (t, $J = 7.3$ Hz, 18H, -CH$_2$CH$_2$CH$_3$).

$p$-C$_2$P$_2$ (378 mg, yield: 54%). $^1$H NMR (400 MHz, CDCl$_3$, ppm, δ): 7.25-7.34 (m, 60H, -SCH$_2$Ph), 6.51 (s, 2H, -CH=CH$_2$), 5.26 (t, $J = 1.0$ Hz, 2H, -CH(-O-)C-), 3.70-3.74 (m, 27H, -SCH$_2$Ph, -SCH(C=O)CH$_2$-), 3.59 (dt, $J = 13.1$, 7.5 Hz,8H, -NCH$_2$CH$_2$-), 3.14, 3.05 (m, 6H, -CHCH$_2$(C=O)-), 2.97 (t, $J = 7.1$ Hz, 2H, CH$_3$(O=C)SCH$_2$H$_2$-), 2.85 (s, 2H, -CH(-C=O)CH$_2$-), 2.47-2.63 (m, 110H, -CH$_2$SCH$_2$-, -CH$_2$SCH$_2$-), 2.34 (s, 3H, CH$_3$(O=C)-SCH$_2$CH$_2$-), 1.86 (m, 16H, -CH$_2$CH$_2$CH$_2$S-), 1.56 (m, 24H, -CH$_2$CH$_2$CH$_3$), 1.42 (m, 24H, -CH$_2$CH$_2$CH$_3$), 1.02 (m, 64H, -SiCH$_2$CH$_2$-), 0.93 (t, $J = 7.7$ Hz, 36H, -CH$_2$CH$_2$CH$_3$).

$p$-C$_4$P$_4$ (161 mg, yield: 46%). $^1$H NMR (400 MHz, CDCl$_3$, ppm, δ): 7.23-7.34 (m, 120H, -SCH$_2$Ph), 6.52 (s, 2H, -CH=CH$_2$), 5.23 (t, $J = 1.0$ Hz, 2H, -CH(-O-)C-), 3.70-3.74 (m, 55H, -SCH$_2$Ph, -SCH(C=O)CH$_2$-), 3.60 (dt, $J = 13.1$, 7.5 Hz, 16H, -NCH$_2$CH$_2$-), 3.14, 3.05 (m, 14H, -CHCH$_2$(C=O)-), 2.99 (t, $J = 7.9$ Hz, 2H, CH$_3$(O=C)SCH$_2$H$_2$-), 2.84 (s, 2H, -CH(-C=O)CH$_2$-), 2.43-2.63 (m, 222H, -CH$_2$SCH$_2$-, -CH$_2$SCH$_2$-), 2.32 (s, 3H, CH$_3$(O=C)-SCH$_2$CH$_2$-), 1.85 (m, 32H, -CH$_2$CH$_2$CH$_2$S-), 1.54 (m, 48H, -CH$_2$CH$_2$CH$_3$), 1.42 (m, 48H, -CH$_2$CH$_2$CH$_3$), 1.05 (m, 128H, -SiCH$_2$CH$_2$-), 0.91 (t, $J = 7.1$ Hz, 72H, -CH$_2$CH$_2$CH$_3$).

$p$-C$_8$P$_8$ (37 mg, yield: 34%). $^1$H NMR (400 MHz, CDCl$_3$, ppm, δ): 7.25-7.35 (m, 240H, -SCH$_2$Ph), 6.51 (s, 2H, -CH=CH$_2$), 5.22 (t, $J = 1.0$ Hz, 2H, -CH(-O-)C-), 3.68-3.74 (s, 111H, -SCH$_2$Ph, -SCH(C=O)CH$_2$-), 3.58 (dt, $J = 14.1$, 7.1 Hz, 32H, -NCH$_2$CH$_2$-), 3.14, 3.05 (m, 30H, -CHCH$_2$(C=O)-), 2.98 (t, $J = 6.9$ Hz, 2H,
CH₃(O=CSCH₂CH₂), 2.84 (s, 2H, -CH(-C=O)CH₂), 2.47-2.63 (m, 44H, -CH₂SCH₂, -CH₂SCH₂), 2.33 (s, 3H, CH₃(O=C)SCH₂CH₂), 1.87 (m, 64H, -CH₂CH₂CH₂S-), 1.55 (m, 96H, -CH₂CH₂CH₃), 1.43 (m, 96H, -CH₂CH₂CH₃), 1.03 (m, 256H, -SiCH₂CH₂), 0.94 (t, J = 7.6 Hz, 144H, -CH₂CH₂CH₃).

3.4 Discrete Amphiphilic Block Polymeric Chains p-CₙD

3.4.1 V₇POSS-SH

Scheme S4. Synthesis of VPOSS-SH: (i) CBr₄, PPh₃, CH₂Cl₂, 0 ºC, 2 h; (ii) potassium thioacetate, KI, MeOH/CH₂Cl₂, 75 ºC, 12 h; (iii) acetyl chloride, MeOH/CH₂Cl₂, -78 ºC, 7h.

V₇POSS-OH (3.63g, 5.0 mmol) was dissolved in anhydrous CH₂Cl₂ (50 mL) in a 100 mL round-bottom flask. CBr₄ (3.36 g, 10.0 mmol) was added to the mixture, and the mixture was transferred into an ice bath. When completely dissolved, PPh₃ (2.62 g, 10.0 mmol) was slowly added. After stirring for 4 hours at room temperature, 20 mL of MeOH, KI (20 mg), and potassium thioacetate (0.23g, 2.0 mmol) were added, and the mixture was further stirred at 75 ºC for 12 h under argon atmosphere. The solvent was then removed under vacuum and the crude product was purified by silica gel column chromatography with PE/DCM (10/1, v/v) as eluent to afford compound 2 as a white powder (3.56 g, yield: 91 %).

Compound 2 (3.00 g, 3.8 mmol) was dissolved in 20 mL of MeOH and 60 mL of CH₂Cl₂ in a 250 mL two-neck round-bottom flask. The mixture was cooled to -78 ºC. Acetyl chloride (15.0 mL, 111 mmol) was then added dropwise to the solution. After further stirring for 14 h at room temperature, the reaction mixture was quenched with 20 mL of water and washed with 30 mL of saturated NaHCO₃ (aq.). The organic layers were combined and washed with 50 mL of water and dried with anhydrous Na₂SO₄. DCM was removed under
vacuum to afford V₇POSS-SH as a white powder (2.5 g, yield: 85%).

3.4.2  p-CₙV (scheme S3). We prepared a library of homopolymeric chains (p-Cₙ, n = 1, 2, 3, 4, 5, 6, 8,16) in addition to those have been described in Section 3.2. The deprotection of the maleimide group (p-Mal-C₁, p-Mal-C₂, p-Mal-C₃, p-Mal-C₄, p-Mal-C₅, p-Mal-C₆, p-Mal-C₈) follows similar approach described above.

**Scheme S5.** Synthetic Route of Amphiphilic Block Polymeric Chains p-CₙV: (i) Toluene, 110 °C, 5 h; (ii) V₇POSS-SH, TEA, CHCl₃, 25 °C, 8 h; (iii) 1-thioglycerol, DMPA, THF, 25 °C, 365 nm × 30 min.

p-Mal-C₁ (200 mg, n = 1, 2, 3, 4, 5, 6, 8) and V₇POSS-SH (3 eq.) were dissolved in 10 mL of anhydrous CHCl₃ in a 25 mL two-neck round-bottom flask, TEA (0.1 mL, 0.73 mmol) was added dropwise to the solution and the mixture was stirred for 24 h. The reaction mixture was quenched with 15 mL of water and washed with 10 mL of saturated NaHCO₃ (aq.). The combined organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated to afford the crude product which was purified by recycling preparative SEC to give the p-CₙV as colorless oil liquid (170 mg~180 mg, yield: 77% ~ 82%).

p-C₁V (180 mg, yield: 82%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.89-6.14 (m, 21H, CH=CH₂), 3.73 (dd, J = 9.0, 3.6 Hz, 1H, -SCH(C=O)CH₂-), 3.63 (t, J = 7.2 Hz, 2H, -NCH₂CH₂-), 3.14, 3.05 (m, 2H, -CH₂SC₂H₇(C=O)-), 2.98 (t, J = 7.2 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 38H, -CH₂SCH₂-, -CH₂SCH₂-), 2.35 (s, 3H, CH₃(O=O)SCH₂CH₂-), 1.86 (m, 6H, -CH₂CH₂CH₂S-), 1.57 (m, 12H, -CH₂CH₂CH₃), 1.43 (m,
12H, -CH₂CH₂CH₃), 1.03 (m, 18H, -SiCH₂CH₂-), 0.93 (t, J = 7.2 Hz, 18H, -CH₂CH₂CH₃).

**p-C₃V** (178 mg, yield: 81%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.85-6.15 (m, 21H, CH₂=CH-), 3.74 (dd, J = 9.3, 3.6 Hz, 2H, -SCH(C=O)CH₂-), 3.64 (t, J = 7.2 Hz, 4H, -NCH₂CH₂-), 3.14, 3.05 (m, 4H, -CHCH₂(C=O)-), 2.96 (t, J = 7.2 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 72H, -CH₂SCH₂-, -CH₂SCH-), 2.34 (s, 3H, CH₃(O=C-)SCH₂CH₂-), 1.85 (m, 10H, -CH₂CH₂CH₂S-), 1.53 (m, 24H, -CH₂CH₂CH₃), 1.45 (m, 24H, -CH₂CH₂CH₃), 1.04 (m, 34H, -SiCH₂CH₂-), 0.96 (t, J = 7.9 Hz, 36H, -CH₂CH₂CH₃).

**p-C₃V** (176 mg, yield: 81%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.83-6.13 (m, 21H, CH₂=CH-), 3.72 (dd, J = 9.6, 3.2 Hz, 3H, -SCH(C=O)CH₂-), 3.67 (t, J = 7.4 Hz, 6H, -NCH₂CH₂-), 3.14, 3.05 (m, 6H, -CHCH₂(C=O)-), 2.92 (t, J = 7.2 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 106H, -CH₂SCH₂-, -CH₂SCH-), 2.36 (s, 3H, CH₃(O=C-)SCH₂CH₂-), 1.84 (m, 14H, -CH₂CH₂CH₂S-), 1.54 (m, 36H, -CH₂CH₂CH₃), 1.47 (m, 36H, -CH₂CH₂CH₃), 1.03 (m, 50H, -SiCH₂CH₂-), 0.94 (t, J = 7.9 Hz, 54H, -CH₂CH₂CH₃).

**p-C₄V** (175 mg, yield: 80%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.83-6.15 (m, 21H, CH₂=CH-), 3.71 (dd, J = 9.1, 3.8 Hz, 4H, -SCH(C=O)CH₂-), 3.62 (t, J = 7.1 Hz, 8H, -NCH₂CH₂-), 3.14, 3.05 (m, 8H, -CHCH₂(C=O)-), 2.99 (t, J = 7.2 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 140H, -CH₂SCH₂-, -CH₂SCH-), 2.32 (s, 3H, CH₃(O=C-)SCH₂CH₂-), 1.83 (m, 18H, -CH₂CH₂CH₂S-), 1.52 (m, 48H, -CH₂CH₂CH₃), 1.44 (m, 48H, -CH₂CH₂CH₃), 1.03 (m, 66H, -SiCH₂CH₂-), 0.92 (t, J = 7.2 Hz, 72H, -CH₂CH₂CH₃).

**p-C₅V** (172 mg, yield: 78%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.81-6.14 (m, 21H, CH₂=CH-), 3.70 (dd, J = 9.5, 3.8 Hz, 5H, -SCH(C=O)CH₂-), 3.62 (t, J = 7.3 Hz, 10H, -NCH₂CH₂-), 3.14, 3.05 (m, 10H, -CHCH₂(C=O)-), 2.96 (t, J = 7.3 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 174H, -CH₂SCH₂-, -CH₂SCH-), 2.31 (s, 3H, CH₃(O=C-)SCH₂CH₂-), 1.81 (m, 22H, -CH₂CH₂CH₂S-), 1.52 (m, 60H, -CH₂CH₂CH₃), 1.43 (m, 60H, -CH₂CH₂CH₃), 1.06 (m, 82H, -SiCH₂CH₂-), 0.91 (t, J = 7.9 Hz, 90H, -CH₂CH₂CH₃).

**p-C₆V** (170 mg, yield: 77%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.87-6.18 (m, 21H, CH₂=CH-), 3.73 (dd, J = 9.5, 3.8 Hz, 6H, -SCH(C=O)CH₂-), 3.62 (t, J = 7.3 Hz, 12H, -NCH₂CH₂-), 3.14, 3.05 (m, 12H, -
CHCH₂(C=O)-), 2.92 (t, J = 7.3 Hz, 2H, CH₃(O=CH₂SCH₂CH₃)), 2.51-2.65 (m, 208H, -CH₂SCH₃, -CH₂SCH₃), 2.39 (s, 3H, CH₃(O=CH₂SCH₂CH₃)), 1.82 (m, 26H, -CH₂CH₂CH₂S-), 1.537 (m, 72H, -CH₃CH₂CH₃), 1.41 (m, 72H, -CH₂CH₂CH₃), 1.06 (m, 98H, -SiCH₂CH₃), 0.91 (t, J = 7.9 Hz, 108H, -CH₂CH₂CH₃).

**p-C₅V** (170 mg, yield: 77%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 5.81-6.11 (m, 21H, CH₂=CH₂), 3.72 (dd, J = 9.5, 3.8 Hz, 8H, -SCH(CH=CH₂)), 3.62 (t, J = 7.3 Hz, 16H, -NCH₂CH₂-), 3.14, 3.05 (m, 16H, -CHCH₂(C=O)-), 2.92 (t, J = 7.3 Hz, 2H, CH₃(O=CH₂SCH₂CH₃)), 2.51-2.65 (m, 276H, -CH₂SCH₃, -CH₂SCH₃), 2.33 (s, 3H, CH₃(O=CH₂SCH₂CH₃)), 1.86 (m, 34H, -CH₂CH₂CH₂S-), 1.54 (m, 96H, -CH₂CH₂CH₃), 1.43 (m, 96H, -CH₂CH₂CH₃), 1.04 (m, 130H, -SiCH₂CH₃), 0.93 (t, J = 7.9 Hz, 144H, -CH₂CH₂CH₃).

**3.4.3 p-C₅D.** A typical procedure is described as follows: **p-C₅V**, 1-thioglycerol (2 eq. to vinyl group), and DMPA (0.03 eq.) were dissolved in 4 mL of THF. The solution was irradiated under 365 nm UV light in a UV reactor for 35 min. The solution is concentrated and purified by recycling preparative SEC to give the **p-C₅D** as colorless oil liquid with 70% - 85% yield.

**p-C₅D** (153 mg, yield: 82%). ¹H NMR (400 MHz, CDCl₃, ppm, δ): 3.71-3.82 (m, 22H, -CH(HOR)CH₂OH, -SCH(CH=CH₂)), 3.57 (t, J = 7.0 Hz, 2H, -NCH₂CH₂-), 3.14, 3.05 (m, 2H, -CHCH₂(C=O)-), 2.96 (t, J = 7.9 Hz, 2H, CH₃(O=CH₂SCH₂CH₃)), 2.51-2.72 (m, 66H, -CH₂SCH₃, -CH₂SCH₃), 2.35 (s, 3H, CH₃(O=CH₂SCH₂CH₃)), 1.86 (m, 6H, -CH₂CH₂CH₂S-), 1.57 (m, 12H, -CH₂CH₂CH₃), 1.43 (m, 12H, -CH₂CH₂CH₃), 1.04 (m, 32H, -SiCH₂CH₃), 0.93 (t, J = 7.1 Hz, 18H, -CH₂CH₂CH₃).

**p-C₅D** (142 mg, yield: 80%). ¹H-NMR (400 MHz, CDCl₃, ppm, δ): 3.70-3.82 (m, 23H, -CH(OH)CH₂OH, -SCH(CH=CH₂)), 3.58 (t, J = 7.0 Hz, 4H, -NCH₂CH₂-), 3.13, 3.05 (m, 4H, -CHCH₂(C=O)-), 2.98 (t, J = 7.0 Hz, 2H, CH₃(O=CH₂SCH₂CH₃)), 2.51-2.65 (m, 100H, -CH₂SCH₃, -CH₂SCH₃), 2.35 (s, 3H, CH₃(O=CH₂SCH₂CH₃)), 1.87 (m, 10H, -CH₂CH₂CH₂S-), 1.57 (m, 24H, -CH₂CH₂CH₃), 1.44 (m, 24H, -CH₂CH₂CH₃), 1.03 (m, 48H, -SiCH₂CH₃), 0.93 (t, J = 7.0 Hz, 36H, -CH₂CH₂CH₃).
**Supporting Information**

**p-C₅D** (139 mg, yield: 78%). ¹H NMR 400 MHz, CDCl₃, ppm, δ: 3.61-3.86 (m, 24H, -CH(OH)CH₂OH, -SCH(C=O)CH₂-), 3.61 (t, J = 7.0 Hz, 6H, -NCH₂CH₂-), 3.14, 3.05 (m, 6H, -CHCH₃(C=O)-), 2.99 (t, J = 7.0 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.63 (m, 134H, -CH₂SCH₂-, -CH₃SCH₂-), 2.32 (s, 3H, CH₃(O=C)-SCH₂CH₂-), 1.87 (m, 14H, -CH₂CHCH₂S-), 1.53 (m, 36H, -CH₂CH₂CH₃), 1.47 (m, 36H, -CH₂CH₂CH₃), 1.04 (m, 64H, -SiCH₂CH₂-), 0.91 (t, J = 7.0 Hz, 54H, -CH₂CH₂CH₃).

**p-C₆D** (137 mg, yield: 77%). ¹H NMR 400 MHz, CDCl₃, ppm, δ: 3.67-3.81 (m, 25H, -CH(OH)CH₂OH, -SCH(C=O)CH₂-), 3.61 (t, J = 7.0 Hz, 8H, -NCH₂CH₂-), 3.14, 3.05 (m, 8H, -CHCH₃(C=O)-), 2.92 (t, J = 7.0 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 168H, -CH₂SCH₂-, -CH₃SCH₂-), 2.39 (s, 3H, CH₃(O=C)-SCH₂CH₂-), 1.81 (m, 18H, -CH₂CHCH₂S-), 1.54 (m, 48H, -CH₂CH₂CH₃), 1.47 (m, 48H, -CH₂CH₂CH₃), 1.03 (m, 80H, -SiCH₂CH₂-), 0.97 (t, J = 7.0 Hz, 72H, -CH₂CH₂CH₃).

**p-C₇D** (129 mg, yield: 75%). ¹H NMR 400 MHz, CDCl₃, ppm, δ: 3.71-3.82 (m, 26H, -CH(OH)CH₂OH, -SCH(C=O)CH₂-), 3.63 (t, J = 7.0 Hz, 10H, -NCH₂CH₂-), 3.14, 3.05 (m, 10H, -CHCH₃(C=O)-), 2.98 (t, J = 7.0 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 102H, -CH₂SCH₂-, -CH₃SCH₂-), 2.35 (s, 3H, CH₃(O=C)-SCH₂CH₂-), 1.86 (m, 22H, -CH₂CHCH₂S-), 1.57 (m, 60H, -CH₂CH₂CH₃), 1.43 (m, 60H, -CH₂CH₂CH₃), 1.03 (m, 96H, -SiCH₂CH₂-), 0.93 (t, J = 7.0 Hz, 90H, -CH₂CH₂CH₃).

**p-C₈D** (122 mg, yield: 72%). ¹H NMR 400 MHz, CDCl₃, ppm, δ: 3.71-3.82 (m, 27H, -CH(OH)CH₂OH, -SCH(C=O)CH₂-), 3.64 (t, J = 7.0 Hz, 12H, -NCH₂CH₂-), 3.14, 3.05 (m, 12H, -CHCH₃(C=O)-), 2.98 (t, J = 7.0 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 236H, -CH₂SCH₂-, -CH₃SCH₂-), 2.36 (s, 3H, CH₃(O=C)-SCH₂CH₂-), 1.83 (m, 26H, -CH₂CHCH₂S-), 1.55 (m, 72H, -CH₂CH₂CH₃), 1.42 (m, 72H, -CH₂CH₂CH₃), 1.07 (m, 112H, -SiCH₂CH₂-), 0.93 (t, J = 7.0 Hz, 108H, -CH₂CH₂CH₃).

**p-C₉D** (119 mg, yield: 70%). ¹H NMR 400 MHz, CDCl₃, ppm, δ: 3.71-3.82 (m, 29H, -CH(OH)CH₂OH, -SCH(C=O)CH₂-), 3.63 (t, J = 7.0 Hz, 16H, -NCH₂CH₂-), 3.14, 3.05 (m, 16H, -CHCH₃(C=O)-), 2.98 (t, J = 7.0 Hz, 2H, CH₃(O=C)SCH₂CH₂-), 2.51-2.65 (m, 304H, -CH₂SCH₂-, -CH₃SCH₂-), 2.35 (s, 3H,
Supporting Information

CH\(_3\)(O=C-)SCH\(_2\)CH\(_2\)-, 1.86 (m, 34H, -CH\(_2\)CH\(_2\)S-), 1.57 (m, 96H, -CH\(_2\)CH\(_2\)CH\(_3\)), 1.43 (m, 96H, -CH\(_2\)CH\(_2\)CH\(_3\)), 1.03 (m, 144H, -SiCH\(_2\)CH\(_2\)), 0.93 (t, \(J = 7.0\) Hz, 144H, -CH\(_2\)CH\(_2\)CH\(_3\)).

3.5 Discrete \(\sigma\)DMS-DPOSS Conjugate (\(S_{13}\)D)

Cl-Si-H (128 g, yiled: 75%): Hexamethylcyclotrisiloxane (120 g, 0.54 mol), dimethylchlorosilane (51 g, 0.54 mol) and acetonitrile (25 mL) was mixed in a 500 ml round-bottom flask in a glove box. DMF (1.5 mL) was then added and the mixture was stirred at room temperature for 72 h. The pure product was obtained by vacuum distillation (the fraction 40-41 °C) as a colorless oil (128 g, 75%).

General synthetic procedure for \(S_x\)-OH: Taking \(S_8\)-OH as an example. In a 250 mL round-bottom flask, Pd/C (0.99 g, 0.93 mmol of Pd) was dispersed in a mixture of dioxane (70 mL) and 1M phosphate buffer (pH = 7, 15 mL). A solution of \(S_8\) (34.1 g, 46.8 mmol) in dioxane (35 mL) was added dropwise to the mixture under ice bath. The solution was then further stirred for another 4 h at room temperature. The mixture was filtrated to remove Pd/C. The aqueous layer was separated and extracted with toluene (100 mL). The organic phases were combined and washed with water (3 \(\times\) 100 mL) and dried with anhydrous MgSO\(_4\). Toluene were removed in vacuo to afford \(S_8\)-OH as a colorless oil (> 95%).

Scheme S6. Synthetic Route of discrete \(\sigma\)DMS: (i) MeSiClH, CH\(_3\)CN, DMF; (ii) Pd/C, 1M PB (pH = 7), dioxane; (iii) pyridine, toluene.
**S₅-OH** (39 g, yield: 98%). \(^1\)H NMR (400 MHz, CDCl₃, ppm, \(\delta\)): 7.35-7.58 (m, 5H, Ar-H), 0.34 (d, \(J = 6.1\) Hz, 6H, ArSi(CH₃)₂-), 0.15 (d, \(J = 3.2\) Hz, 6H, -Si(CH₃)₂OH), 0.07 (m, 18H, -Si(CH₃)₂-).

**S₉-OH** (52g, yield: 98%). \(^1\)H NMR (400 MHz, CDCl₃, ppm, \(\delta\)): 7.35-7.58 (m, 5H, Ar-H), 0.34 (d, \(J = 5.9\) Hz, 6H, ArSi(CH₃)₂-), 0.15 (d, \(J = 2.9\) Hz, 6H, -Si(CH₃)₂OH), 0.07 (m, 66H, -Si(CH₃)₂-).

**General procedure for synthesis of S₅:** Taking S₁₃ as an example. In a glove box, Cl-Si₄-H (14.5 g, 45.6 mmol) was dissolved in toluene (100 mL) in a 500 ml round-bottom flask. S₅-OH (34.0 g, 45.6 mmol) was added dropwise into the mixture in 30 min at 0 °C. The mixture was further stirred for another 4 hours. The reaction mixture was quenched by adding water (100 mL) and toluene (100 mL). The organic phases were collected and washed with water (3 × 100 mL) and dried with anhydrous MgSO₄. Toluene was removed in vacuo to give the crude product, which was purified by vacuum distillation (fraction 200 - 205 °C) to afford S₁₃ as a colorless oil (35.2 g, 75%).

**S₅-H** (40.5 g, yield: 85%). \(^1\)H NMR (400 MHz, CDCl₃, ppm, \(\delta\)): 7.34-7.57 (m, 5H, Ar-H), 4.70 (p, \(J = 2.1\) Hz, 1H, -Si(CH₃)₂H), 0.34 (d, \(J = 6.5\) Hz, 6H, ArSi(CH₃)₂-), 0.19 (d, \(J = 2.9\) Hz, 6H, HSi(CH₃)₂-), 0.07 (m, 18H, -Si(CH₃)₂-).

**S₉-H** (53.1 g, yield: 80%). \(^1\)H NMR (400 MHz, CDCl₃, ppm, \(\delta\)): 7.34-7.57 (m, 5H, Ar-H), 4.70 (p, \(J = 2.4\) Hz, 1H, -Si(CH₃)₂H), 0.34 (d, \(J = 6.2\) Hz, 6H, ArSi(CH₃)₂-), 0.19 (d, \(J = 2.9\) Hz, 6H, HSi(CH₃)₂-), 0.07 (m, 48H, -Si(CH₃)₂-).

**S₁₃-H** (35.2 g, yield: 75%). \(^1\)H NMR (400 MHz, CDCl₃, ppm, \(\delta\)): 7.34-7.57 (m, 5H, Ar-H), 4.70 (p, \(J = 2.8\) Hz, 1H, -Si(CH₃)₂H), 0.34 (d, \(J = 6.9\) Hz, 6H, ArSi(CH₃)₂-), 0.19 (d, \(J = 2.8\) Hz, 6H, HSi(CH₃)₂-), 0.07 (m, 66H, -Si(CH₃)₂-).
**Scheme S7.** Synthetic Route of discrete S$_{13}$D: (i) S$_{13}$-H, B(C$_6$F$_5$)$_3$, DCM; (ii) 1-thioglycerol, AIBN, toluene.

**S$_{13}$V:** In a glove box, S$_{13}$ (0.20 g, 0.20 mmol) and VPOSS-OH (0.16 g, 0.22 mmol) were dissolved in CH$_2$Cl$_2$ (3 mL) in 25 mL round-bottom flask. A solution of B(C$_6$F$_5$)$_3$ (20 mg, 0.04 mmol) in CH$_2$Cl$_2$ (1 mL) was added quickly into the mixture. The mixture was stirred for 15 min at room temperature, and then quenched by adding water (20 mL) and CH$_2$Cl$_2$ (50 mL). The organic phases were washed with water (2 × 50 ml) and dried with MgSO$_4$. CH$_2$Cl$_2$ was removed in vacuo to give the crude product, which was further purified by recycling preparative SEC to give S$_{13}$V as clear, waxy solid (0.29 g, yield: 80 %). $^1$H NMR (400 MHz, CDCl$_3$, ppm, δ): 7.34-7.57 (m, 5H, Ar-H), 5.86-6.13 (m, 21H, CH$_2$=CH-), 3.73 (t, $J$ = 7.0 Hz, 2H, -CH$_2$C$_2$H$_2$OSi(CH$_3$)$_2$-), 2.57-2.65 (m, 4H, -CH$_2$CH$_2$SCH$_2$CH$_2$-), 1.79 (tt, $J$ = 7.0, 6.1 Hz, 2H, -SCH$_2$CH$_2$CH$_2$S(CH$_3$)$_2$-), 0.34 (d, $J$ = 6.9 Hz, 6H, ArS(CH$_3$)$_2$-), 0.05-0.09 (m, 72H, -Si(CH$_3$)$_2$-).

**S$_{13}$D:** In a glove box, S$_{13}$V (0.10 g, 0.057 mmol), 1-thioglycerol (0.0867 g, 0.802 mmol), and AIBN (0.0263 g, 0.160 mmol) were dissolved in toluene (5 mL) in 25 mL round-bottom flask. The mixture was moved out of box and heated to 75 °C for 24 h. Toluene was removed in vacuo to give the crude product, which was purified by recycling preparative SEC to give S$_{13}$D as waxy solid (0.10 g, yield: 65 %). $^1$H NMR (400 MHZ, DMSO, ppm, δ): 7.31-7.51 (m, 5H, Ar-H), 4.51-4.73 (m, 14H, -CH$_2$CH(OH)CH$_2$(OH)), 3.65 (t, $J$ = 7.9 Hz, 2H, -CH$_2$CH$_2$OSi(CH$_3$)$_2$-), 3.52 (m, 7H, -CH$_2$CH(OH)CH$_2$(OH)), 2.39-2.62 (m, 18H, -CH$_2$CH$_2$SCH$_2$CH$_2$-, -CH$_2$CH(OH)CH$_2$(OH)), 1.66 (tt, $J$ = 7.0, 6.1 Hz, 2H, -SCH$_2$CH$_2$CH$_2$S(CH$_3$)$_2$-), 0.95 (m, 16H, -SiCH$_2$CH$_2$-,
4. Detailed Synthesis and Characterizations.

4.1 Preparation of Amphiphilic Block Chains (p-CnD). To conjugate DPOSS moiety onto CPOSS chains, a thiol-functionalized VPOSS (V7POSS-SH) was first prepared (Scheme S4), and then coupled with activated Cn blocks through Michael coupling reaction (labeled as p-CnV). Further decorating the POSS cage with 14 hydroxyl groups via thiol-ene reaction leads to the amphiphilic block chains (p-CnD, Scheme S5). Here we take p-C3D as an example to illustrate the synthetic details. After coupling, the SEC trace of p-C3V shifts clearly towards low retention volume, as compared with the precursor p-C3 (Figure S17b). A single peak was observed in the corresponding MALDI-ToF MS, with molecular mass (5159.43 Da) in good agreement with calculated value (5158.82 Da), confirming the proposed chemical structure with atomic accuracy (Figure S17c). The 1H NMR spectrum of the resultant product (p-C3V) contains signals from both components (Figure S17a). In particular, the typical resonances of vinyl groups appear at 5.8-6.2 ppm. Installation of surface functionalities onto the vinyl groups (p-CnD) proceeds promptly and quantitatively under UV irradiation. As expected, the signals attributed to the vinyl groups disappeared completely, while the resonances of thioglycerol emerge (δ 3.85, 3.12, and 2.74 ppm, Figure S17a). A further shift of the SEC trace confirms the increase of the hydrodynamic volume (Figure S17b). Due to collective hydrogen bonds, partial aggregation exists in the solution among DPOSS cages, as indicated by a shoulder peak in the SEC trace. Due to low ionization efficiency, acquiring a high-quality mass spectrum of p-C3D turned out to be very challenging. Similar situations have also been reported in the literatures.[1] Nevertheless, other complementary characterizations (i.e. NMR and SEC) could provide convincing evidences towards the success of the synthesis. Amphiphilic block chains with varied compositions can be modularly synthesized using corresponding precursors (Figures S18-S20). The molecular
characterizations of this series of discrete molecules are summarized in Table 2.

### 4.2 Preparation of Particle-Polymer Conjugate (Si3D)

Discrete oDMS was synthesized following an iterative exponential growth approach according to literature with slight modification (Scheme S6). End-capping with a VPOSS moiety, and further decorating the periphery of the particle with thioglycerol ligands through thiol-ene reaction leads to the linear polymer-particle conjugate (Si3D, Scheme S7). The chemical structure and discrete feature were fully characterized by a combination of NMR, SEC, and MALDI-ToF MS (Figure S25).

### 5. Equation and calculations

#### 5.1 Volume fraction of CPOSS ($f_c$)

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

$$f_A = \frac{n \cdot M_c / \rho_c}{n \cdot M_c / \rho_c + M_D / \rho_D} \quad (S1)$$

where $M_0$ is the molecular weight of DPOSS (1430.2 g/mol), $M_c$ is the molecular weight of CPOSS (1453.6 g/mol), $n$ is the number of CPOSS, and $\rho_0$ and $\rho_c$ 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 1.05 g/cm$^3$ (assuming the density of CPOSS is similar to that of BPOSS, i.e., POSS with seven isobutyl groups).

#### 5.2 Domain spacing ($d$)

The domain spacing ($d$) is calculated directed from the primary scattering peak ($q_1$) of the SAXS profile:

$$d = \frac{2\pi}{q_1} \quad (S2)$$
5.3 Characteristic dimension of the phase \((a)\).

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

\[
a = d \quad \text{for LAM}
\]

\[
a = \sqrt{6}d \quad \text{for DG}
\]

\[
a = 2d/\sqrt{3} \quad \text{for HEX}
\]

\[
a = \sqrt{2}d \quad \text{for BCC}
\]

5.4 Volume of the monomers

The volume of the monomer can be estimated by the following calculation: \([^5]\)

\[
V = \frac{M}{N_A \rho}
\]

where \(M\) and \(\rho\) are the molecular weight and density of the monomer. \(N_A\) is the Avogadro constant. According to literature, \(M_{\text{CPOSS}} = 1457.6\ \text{g/mol}\), \(M_{\text{oDMS}} = 74\ \text{g/mol}\); \(\rho_{\text{CPOSS}} = 1.05\ \text{g/cm}^3\), \(\rho_{\text{oDMS}} = 0.95\ \text{g/cm}^3\). Plug in the relevant parameters to get: \(V_{\text{CPOSS}} = 2.3\ \text{nm}^3\), \(V_{\text{oDMS}} = 0.13\ \text{nm}^3\).
6. Supplemental Schemes and Figures

Figure S1. Regioisomers of octavinyl POSS with two hydroxyl substituting groups at *para*-, *meta*-, and *ortho*-positions.

Figure S2. $^1$H NMR spectra of *p*-, *m*-, and *o*-V$_6$POSS(OH)$_2$. 
Figure S3. $^{29}$Si NMR spectra of $p$-, $m$-, and $o$-V$_6$POSS(OH)$_2$.

Figure S4. $^1$H NMR spectra of the intermediates of $p$-CPOSS monomer.
Figure S5. MALDI-ToF MS of the intermediates of p-CPOSS monomer.

Figure S6. $^{13}$C NMR spectra of the intermediates of p-CPOSS monomer.
Figure S7. $^{13}$C NMR spectra of the $p$-$C_1$ and $p$-$C_2$.

Figure S8. $^{13}$C NMR spectra of the $p$-FPOSS-monomer (a) and $p$-PPOSS-monomer (b). The red asterisks denotes resonances from residual THF.
Figure S9. $^1$H NMR of the orthogonal deprotection process: $p$-C$_1$ (a), $p$-Mal-C$_1$ (b), and $p$-C$_1$-SH (c).

Figure S10. $^1$H NMR spectra of discrete CPOSS chains with para-configuration ($p$-C$_n$).
Figure S11. Chemical structure (a), $^1$H NMR spectra (b), SEC profiles (c), and MALDI-ToF MS (d) of PPOSS chains ($p$-$P_n$).
**Figure S12.** Chemical structure (a), SEC profiles (b), and $^1$H NMR spectra (c) of FPOSS chains ($p$-$F_n$).
Figure S13. Chemical Structure (a), $^1$H NMR spectra (b), SEC profiles (c), and MALDI-ToF MS (d) of $p$-C$_n$P$_n$ chains.
**Figure S14.** Chemical Structure (a), $^1$H NMR spectra (b), and SEC profiles (c) of $p$-$C_nF_m$ chains.
Figure S15. SAXS profiles of $p$-C$_2$P$_2$ (a) and $p$-C$_4$F$_4$ (b) at room temperature.

Figure S16. $^1$H NMR spectra of V$_3$POSS-SH and its precursors.
Figure S17. $^1$H NMR spectra (a), SEC profiles (b), and MALDI-ToF MS (c) of $p$-C$_n$D (take $n = 3$ as an example).
Figure S18. $^1$H NMR spectra of $p$-$C_nV$ with varied number of repeat units.

Figure S19. $^1$H NMR spectra of $p$-$C_nD$ with varied number of repeat units.
Figure S20. SEC profiles of $p$-$C_nV$ (a) and $p$-$C_nD$ (b).

Figure S21. TGA curves of $p$-$C_4$ (a) and $p$-$C_8D$ (b). Heating rate: 10 °C/min.
Figure S22. DSC thermograms of the $p$-$C_n$ in the cooling (a) and heating (b) cycle. Heating/cooling rate: 5 °C/min.

Figure S23. DSC thermograms of the $p$-$C_n$D in the cooling (a) and heating (b) cycle. Heating/cooling rate: 5 °C/min.
Figure S24. SAXS patterns of \( p\)-C\(_8\)D (a), \( m\)-C\(_8\)D (b), and \( o\)-C\(_8\)D (c).

Figure S25. \(^1\)H NMR spectra (a), SEC profiles (b), and MALDI-ToF MS (c) of S\(_{13}\)D and its precursors.
Figure S26. Temperature dependent SAXS profiles of the amphiphilic POSS chains: \( p\text{-C}_1\text{D} \) (a), \( p\text{-C}_2\text{D} \) (b), \( p\text{-C}_3\text{D} \) (c), \( p\text{-C}_4\text{D} \) (d), \( p\text{-C}_5\text{D} \) (e), and \( p\text{-C}_6\text{D} \) (f).
Figure S27. Temperature dependent SAXS profiles of the polymer-particle conjugate S13D.
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