

Giant Gemini Surfactants Based on Polystyrene-Hydrophilic Polyhedral Oligomeric Silsesquioxane Shape Amphiphiles: Sequential “Click” Chemistry and Solution Self-Assembly

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Experimental Section

Chemicals and Solvents. Styrene monomers (Aldrich, 99 %,) were purified by distillation from calcium hydride under reduced pressure prior to use. Tetrahydrofuran (THF, EM Science, Certified ACS), methanol (Fisher Scientific, reagent grade), ethyl acetate (Fisher Scientific, ACS grade), toluene (Fisher Scientific, Certified ACS), dichloromethane (Fisher Scientific, Certified ACS), chloroform (Fisher Scientific, Certified ACS), *N, N*-dimethylformamide (DMF, Sigma-Aldrich, anhydrous 99.8 %) and hexanes (Fisher Scientific, Certified ACS) were used after distillation. Cuprous bromide (CuBr, Aldrich, 98 %) was freshly purified by stirring in acetic acid overnight, washed with acetone, and dried in vacuum. Octavinyl POSS (VPOSS, Hybrid Plastics, > 97 %), *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA, Aldrich, 99 %), 2-bromoisobutyryl bromide (Aldrich, 98 %), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99 %), 1-thioglycerol (Sigma, > 99 %), 4-pentynoic acid (Acros Organics, 98%), *N, N'*-diisopropylcarbodiimide (DIPC, Acros Organics, 99 %), 4-(dimethylamino) pyridine (Aldrich, 99 %), sodium azide (Aldrich, > 99 %), terephthalic acid (Aldrich, 98 %), biphenyl-4,4'-dicarboxylic acid (Aldrich, 98 %) were used as received. 2-Mercaptoacetic acid (Aldrich, > 98 %) was distilled under reduced pressure before use. Silica gel (VWR, 230-400 mesh) was activated by heating to 140 °C for 12 hrs. 4-(Dimethylamino) pyridinium toluene-*p*-sulfonate (DPTS), azido-end-capped polystyrene (PS-N₃) and HO-(VPOSS)-OH were synthesized as reported.^{25, 26}

Characterization. Size exclusion chromatographic analyses (SEC) for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10³/10⁴ Å), mixed bed (10³, 10⁴, 10⁶ Å)], and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential

viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C.

All ^1H , ^{13}C and ^{29}Si NMR spectra were acquired in CDCl_3 (Aldrich, 99.8 % D) utilizing a Varian Mercury 300 NMR and 500 NMR spectrometer. The ^1H NMR spectra were referenced to the residual proton signals in the CDCl_3 at δ 7.27 ppm; while the ^{13}C NMR spectra were referenced to $^{13}\text{CDCl}_3$ at δ 77.00 ppm. And the ^{29}Si NMR spectra were referenced to tetramethylsilane in the CDCl_3 at δ 0 ppm.

Infrared spectra were obtained on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting films on KBr plates from solutions with subsequent drying at 40 - 50 °C. The spectroscopic data were processed using Win-IR software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All of the spectra were measured in positive reflection or linear mode. The instrument was calibrated prior to each measurement with external PMMA or PS standards at the molecular weight under consideration. The compound *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Santa Cruz Biotechnology, Inc., >99 %) served as matrix and was prepared in CHCl_3 at a concentration of 20 mg/mL. Cationizing agent of sodium trifluoroacetate or silver trifluoroacetate was prepared in $\text{MeOH}/\text{CHCl}_3$ (v/v = 1/3) at a concentration of 5 mg/mL or 10 mg/mL. All the samples were dissolved in CHCl_3 with a ratio of 10/1 (v/v) for the matrix and salt. The sample preparation followed the procedure of depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry

matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample (the sandwich method). After solvent evaporation, the plate was inserted into the MALDI spectrometer. The attenuation of the Nd:YAG laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity.

Thin-layer chromatographic analyses of the functionalized polymers were carried out by spotting samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator) and developing using toluene or its mixture with other polar solvents.

Dynamic light scattering (DLS) experiments were conducted using a Brookhaven Instrument coupled with a Bi-200SM goniometer, BI-9000AT correlator, and an EMI-9863 photomultiplier tube for photo counting. A Meller Griot 35 mW He-Ne laser was used as the light source (632.8 nm). A cylindrical glass scattering cell with diameter of 12 mm was placed at the center of a thermostatic bath ($\pm 0.01\text{ }^{\circ}\text{C}$) with decahydronaphthalene used for refractive index matching. Correlation functions at 90° and other angles were recorded at $25\text{ }^{\circ}\text{C}$. The intensity-intensity time-correlation function $G^{(2)}(t)$ of the distributed object in self-beating mode was measured. It was related to the normalized first-order electric field time correlation function $g^{(1)}(t)$. A Laplace inversion program, CONTIN, was applied to analyze $g^{(1)}(t)$ to obtain the hydrodynamic radius, R_h , and its distribution.

Bright field images of transmission electron microscope (TEM) were recorded in a JEOL-1230 microscope with an accelerating voltage of 120 kV. 10 μL of the micelle solutions were deposited onto carbon coated copper grids. After ca. 3 min, the excess solution was wicked away by a piece of filter paper. The sample was then allowed to dry under ambient conditions. TEM images were recorded on a digital CCD camera and processed with the accessory digital imaging system.

Synthetic Procedures.

Yne-(VPOSS)-OH. To a 250 mL round-bottomed flask equipped with a magnetic stirring bar was added HO-(VPOSS)-OH (741 mg, 1.0 mmol), 4-pentynoic acid (98 mg, 1.0 mmol) and DPTS (295 mg, 1.0 mol), followed by the addition of 120 mL freshly dried CH₂Cl₂ to fully dissolve the solids. The mixture was capped by a rubber septum, cooled to 0 °C and stirred at that temperature for 10 min, and then DIPC (189 mg, 1.5 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hours. The white precipitation was then filtered off and the filtrate was washed with water and brine, dried over Na₂SO₄. After solvent removal, the residue was purified by flash chromatography on silica gel using CH₂Cl₂ as the eluent to afford the product as a white powder (410 mg, 50 %). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 6.16-5.86 (m, 21H, -CH=CH₂), 4.27-4.14 (m, 2H, -CH(OH)CH₂O-), 3.94 (m, 1H, -CH(OH)CH₂O-), 2.78-2.49 (m, 8H, -CH₂SCH₂- & CH₂CH₂C≡CH), 1.99 [t, 1H, -C≡CH], 1.10 (t, 2H, -SiCH₂-). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 171.76, 137.20, 128.70, 82.51, 69.35, 68.06, 67.31, 35.88, 33.40, 26.70, 14.55, 13.32. FT-IR (KBr) ν (cm⁻¹): 1740 (C=O), 1107 (O-Si-O). MS (MALDI-TOF): Calcd. for C₂₄H₃₆NaO₁₅SSi₈ 842.98, Found: 842.34 (M·Na)⁺.

Yne-(VPOSS)₂-Yne-1. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar was added Yne-(VPOSS)-OH (400 mg, 0.487 mmol), terephthalic acid (38 mg, 0.230 mmol) and DPTS (147 mg, 0.500 mol), followed by the addition of 20 mL freshly dried DMF. The mixture was capped by a rubber septum, cooled to 0 °C and stirred at that temperature for 10 min, and then DIPC (126 mg, 1.00 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 72 hours. DMF was evaporated under vacuum and CH₂Cl₂ was used to dissolve the crude sample. The white precipitate was then filtered off and the filtrate was

washed with water and brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as the eluent to afford the product as a white powder (130 mg, 32 %). ^1H NMR (300 MHz, CDCl_3 , ppm, δ): 8.09 (s, 4H, aromatic), 6.16-5.86 (m, 42H, $-\text{CH}=\text{CH}_2$), 5.39 (m, 2H, $-\text{CH}(\text{OR})\text{CH}_2\text{O}-$), 4.55 (m, 2H, $-\text{CH}(\text{OR})\text{CH}_2\text{O}-$), 4.43 (m, 2H, $-\text{CH}(\text{OR})\text{CH}_2\text{O}-$), 2.88 (t, 4H, $-\text{SCH}_2\text{CH}-$), 2.73 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{S}-$), 2.60-2.46 (m, 8H, $-\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$), 1.95 [t, 2H, $-\text{C}\equiv\text{CH}$], 1.10 (t, 4H, $-\text{SiCH}_2-$). ^{13}C NMR (75 MHz, CDCl_3 , ppm, δ): 171.29, 164.89, 137.12, 133.78, 128.59, 82.19, 71.57, 69.24, 63.93, 33.19, 31.91, 26.80, 14.32, 13.09. FT-IR (KBr) ν (cm^{-1}): 1732 (C=O), 1110 (O-Si-O). MS (MALDI-TOF): Calcd. for $\text{C}_{56}\text{H}_{74}\text{NaO}_{32}\text{S}_2\text{Si}_{16}$ 1792.98, Found: 1793.13 ($\text{M}+\text{Na}$) $^+$.

Yne-(VPOSS)₂-Yne-2. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar was added Yne-(VPOSS)-OH (400 mg, 0.487 mmol), biphenyl-4,4'-dicarboxylic acid (56 mg, 0.230 mmol) and DPTS (147 mg, 0.500 mol), followed by the addition of 20 mL freshly dried DMF. The mixture was capped by a rubber septum, cooled to 0 °C and stirred at that temperature for 10 min, and then DIPC (126 mg, 1.00 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 72 hours to complete the reaction. DMF was then evaporated under vacuum and CH_2Cl_2 was used to dissolve the crude sample. The white precipitate was also filtered off and the filtrate was washed with water and brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as the eluent to afford the product as a white powder (163 mg, 39 %). ^1H NMR (300 MHz, CDCl_3 , ppm, δ): 8.15 (d, 4H, aromatic), 7.71 (d, 4H, -aromatic), 6.16-5.86 (m, 42H, $-\text{CH}=\text{CH}_2$), 5.41 (m, 2H, $-\text{CH}_2\text{CH}(\text{OCO})-$), 4.57 (m, 2H, $-\text{CH}(\text{OCO})\text{CH}_2\text{O}-$), 4.44 (m, 2H, $-\text{CH}(\text{OCO})\text{CH}_2\text{O}-$), 2.89 (t, 4H, $-\text{SCH}_2\text{CH}-$), 2.73 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{S}-$), 2.60-2.46 (m, 8H,

-CH₂CH₂C≡CH), 1.94 [t, 2H, -C≡CH], 1.12 (t, 4H, -SiCH₂-). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 171.27, 165.39, 144.62, 137.05, 130.39, 128.58, 127.33, 82.23, 71.31, 69.18, 63.86, 33.19, 31.81, 26.89, 14.34, 13.12. FT-IR (KBr) ν (cm⁻¹): 1740 (C=O), 1110 (O-Si-O). MS (MALDI-TOF): Calcd. for C₆₂H₇₈NaO₃₂S₂Si₁₆ 1869.01, Found: 1869.15 (M·Na)⁺.

PS-(VPOSS)₂-PS-1. To a 100 mL Schlenk flask equipped with a magnetic stirring bar was added Yne-(VPOSS)₂-Yne-1 (100 mg, 0.0565 mmol), PS-N₃ (*M*_n = 3.2 kg/mol, PDI = 1.05, 370 mg, 0.116 mmol), CuBr (1 mg, 0.005 mmol), and freshly distilled toluene (10 mL). The resulting solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (20 mg, 0.113 mmol) via pipet. The mixture was then degassed again by one more cycle, and stirred at room temperature for another 24 hours. After the reaction was completed, the solution was directly transferred onto the top of a silica gel column. Pure toluene was first used as the eluent to fully remove the unreacted starting materials, then a mixture of toluene and ethyl acetate (v/v= 1/1) was used to elute the product off the column. After solvent removal, the crude product was precipitated into cold MeOH. After filtration, the sample PS-(VPOSS)₂-PS-1 was collected and dried under vacuum overnight to give a white powder (411 mg; Yield: 91 %). SEC: *M*_n = 8.0 kg/mol, PDI = 1.01.

PS-(VPOSS)₂-PS-2. Same procedure as that for PS-(VPOSS)₂-PS-1 was employed using Yne-(VPOSS)₂-Yne-2 (100 mg, 0.0542 mmol), PS-N₃ (*M*_n = 3.2 kg/mol, PDI = 1.05, 356 mg, 0.111 mmol), CuBr (1 mg, 0.005 mmol), toluene (10 mL) and PMDETA (19 mg, 0.108 mmol). A white powder was obtained (377 mg; Yield: 88 %). SEC: *M*_n = 7.9 kg/mol, PDI = 1.03.

PS-(APOSS)₂-PS-1. PS-(VPOSS)₂-PS-1 (*M*_n = 8.0 kg/mol, 200 mg, 0.025 mmol), 2-mercaptoacetic acid (46 mg, 0.50 mmol), and DMPA (2 mg, 0.005 mmol) were dissolved in 5 mL

of THF, followed by irradiation with UV (365 nm) for 15 minutes. The solution was then precipitated into cold methanol solution three times. The sample PS-(APOSS)₂-PS-1 was collected and dried under vacuum overnight to afford a white powder (176 mg; Yield: 79 %). SEC: M_n = 8.9 kg/mol, PDI = 1.03.

PS-(APOSS)₂-PS-2. Same procedure as that for PS-(APOSS)₂-PS-1 was employed using PS-(VPOSS)₂-PS-2 (M_n = 7.9 kg/mol, 200 mg, 0.025 mmol), 2-mercaptoacetic acid (46 mg, 0.50 mmol), and DMPA (2 mg, 0.005 mmol). PS-(APOSS)₂-PS-2 was obtained as a white powder (189 mg; Yield: 83 %). SEC: M_n = 9.1 kg/mol, PDI = 1.01.

Micelle Preparation. The samples were first dissolved in a common solvent (1,4-dioxane or DMF) and stirred at room temperature overnight to ensure complete dissolution of the polymer to prepare a stock solution at specified concentrations. The solution was then filtered through a filter of 0.22 μ m pore size to remove any dust. Deionized water was filtered through a filter of 0.22 μ m pore size and added dropwise at a rate of 10 μ L/ hour using a syringe pump into a vial containing 2.00 g of the stock solution. Water addition was continued until a final water content of 70 (wt)%. Then the micelle solution was dialyzed against deionized water for three days to remove the common solvent and fix the micellar morphology.

Measurement of Degree of Ionization using FT-IR Spectrometry. To measure the degree of ionization of the carboxylic acids on the POSS cage, micelle solutions were directly freeze-dried under vacuum to obtain solvent-free samples. The freeze-dried sample was ground with KBr powder and pressed into solid disks for FT-IR characterization. The spectra were collected on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) and processed using Win-IR software. Fig. S12 shows the spectra of PS-(APOSS)₂-PS-1 freeze-dried from micelle solutions of various common

solvents. Two distinct vibrational absorption bands for the carbonyl groups of the carboxylic acid groups can be discerned. The one at $\sim 1720\text{ cm}^{-1}$ is attributed to the C=O stretching of native -COOH groups, and the one at $\sim 1600\text{ cm}^{-1}$ is associated with the asymmetric stretching band of the ionized carboxylate (COO^-) group.^{S1,S2} When the common solvent was changed from 1, 4-dioxane to DMF and further to the DMF/NaOH mixture, the COOH band intensity decreased and the COO^- band intensity increased. Qualitatively, it suggests that the acid groups became more ionized. Quantitatively, assuming similar extinction coefficients for the two bands, the degree of ionization (α) can be estimated from the ratio of the intensity of the $\nu(\text{COO}^-)$ peak to the sum of the intensities of the $\nu(\text{COO}^-)$ and $\nu(\text{COOH})$ peaks.

$$\alpha = \frac{I_{\nu(\text{COO}^-)}}{I_{\nu(\text{COO}^-)} + I_{\nu(\text{COOH})}} \times 100\%$$

The degrees of ionization were calculated to be 29 %, 35 %, and 38 %, respectively.

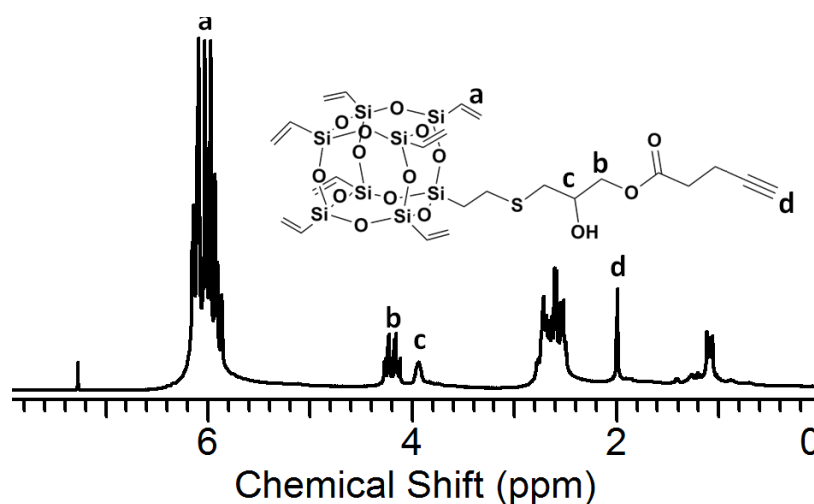


Fig. S1. ^1H NMR spectrum of Yne-(VPOSS)-OH.

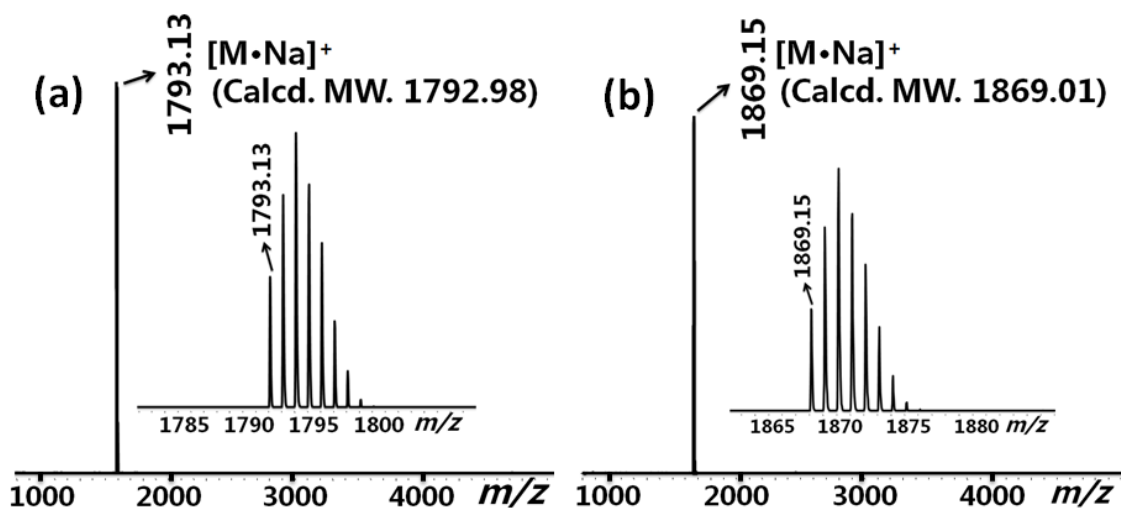


Fig. S2. MALDI-TOF mass spectra of Yne-(VPOSS)₂-Yne-1 (a), and Yne-(VPOSS)₂-Yne-2 (b); the zoom-in views of the spectra are provided in the insets to show the monoisotopic pattern of each peak.

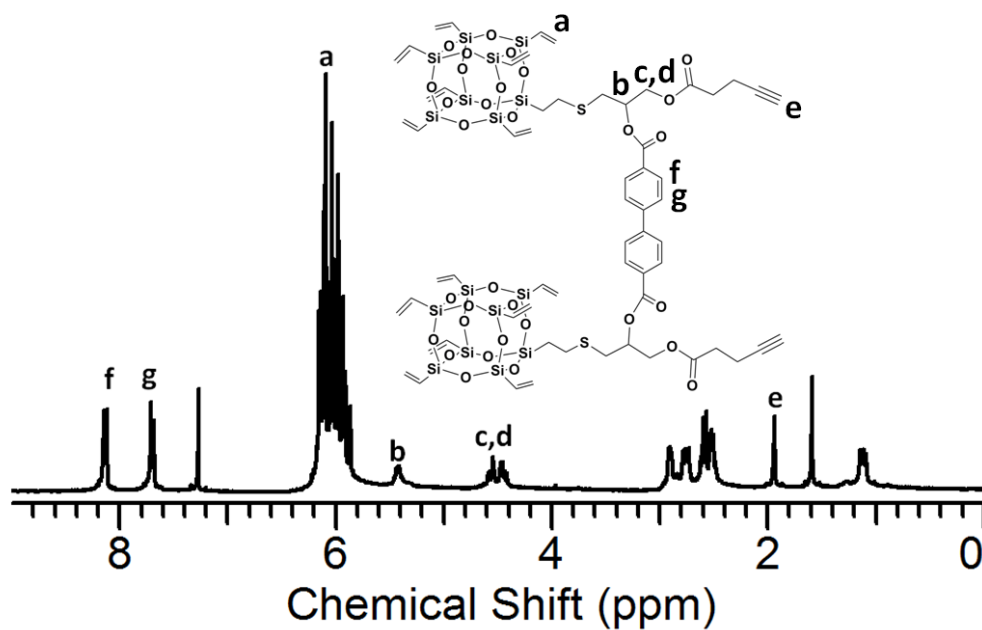


Fig. S3. ¹H NMR spectrum of Yne-(VPOSS)₂-Yne-2.

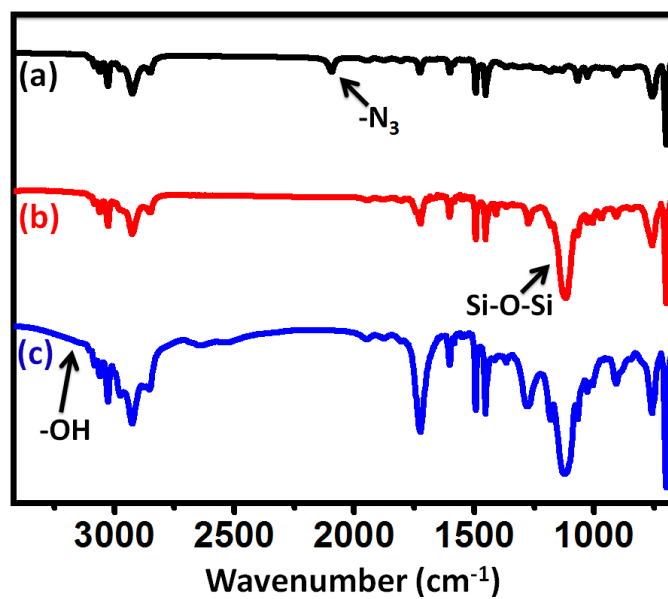


Fig. S4. FTIR spectra of (a) PS-N₃ (black curve), (b) PS-(VPOSS)₂-PS-1 (red curve), and (c) PS-(APOSS)₂-PS-1 (blue curve).

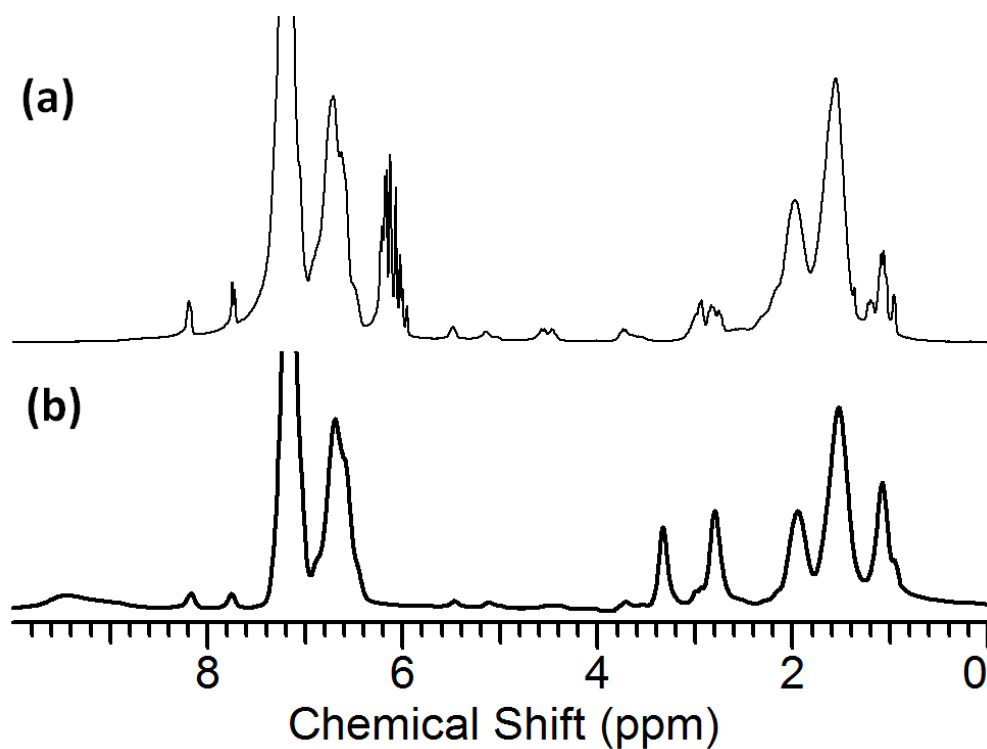


Fig. S5. ¹H NMR spectra of (a) PS-(VPOSS)₂-PS-2, and (b) PS-(APOSS)₂-PS-2.

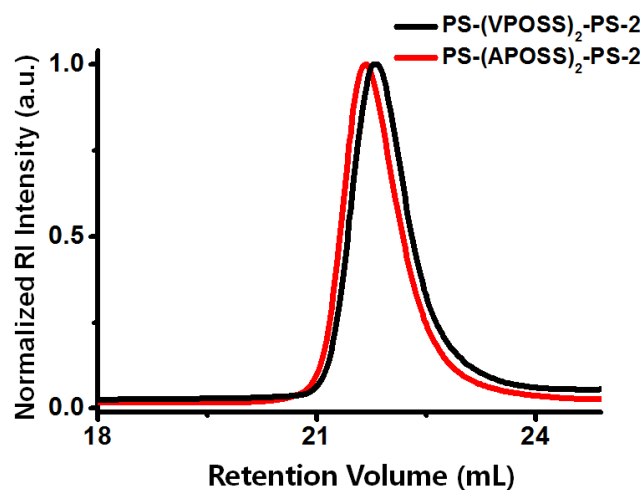


Fig. S6. SEC overlays of PS-(VPOSS)₂-PS-2 (black curve) and PS-(APOSS)₂-PS-2 (red curve).

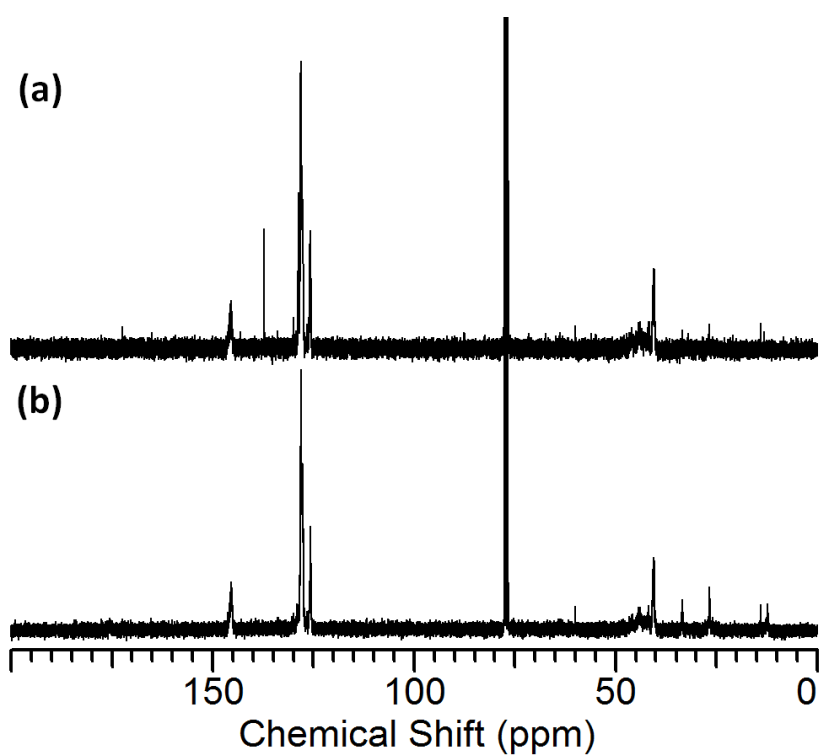


Fig. S7. ¹³C NMR spectra of (a) PS-(VPOSS)₂-PS-1, and (b) PS-(APOSS)₂-PS-1.

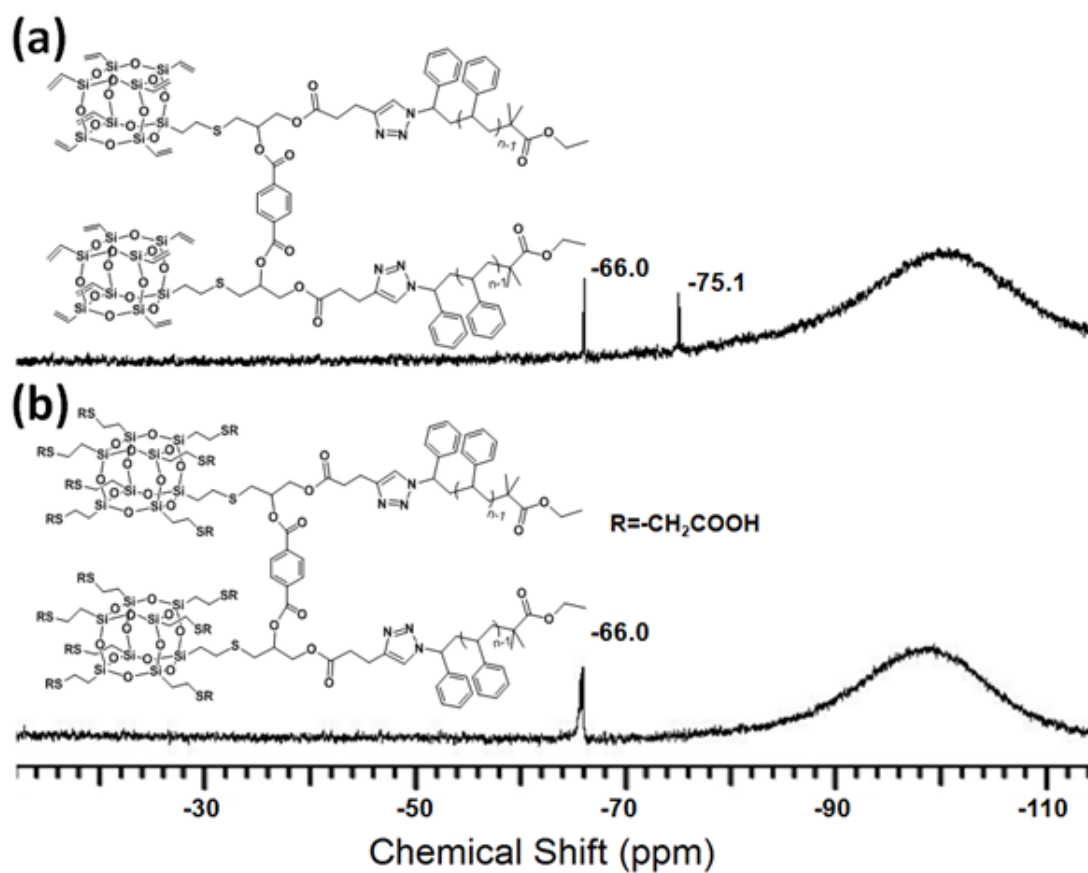


Fig. S8. ^{29}Si NMR spectra of (a) PS-(VPOSS) $_2$ -PS-1, and (b) PS-(APOSS) $_2$ -PS-1.

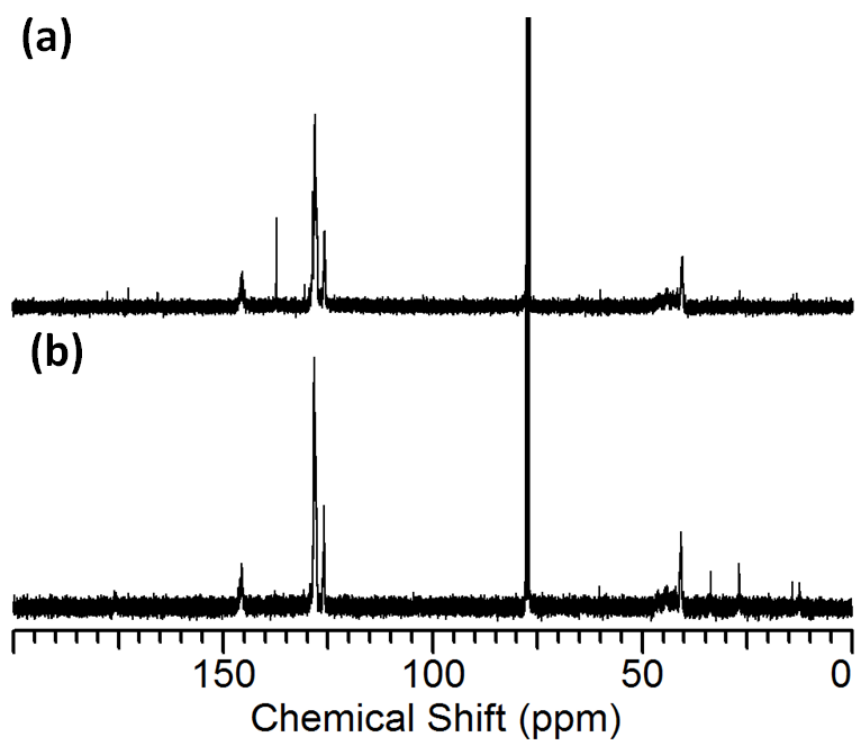


Fig. S9. ^{13}C NMR spectra of (a) PS-(VPOSS) $_2$ -PS-2, and (b) PS-(APOSS) $_2$ -PS-2.

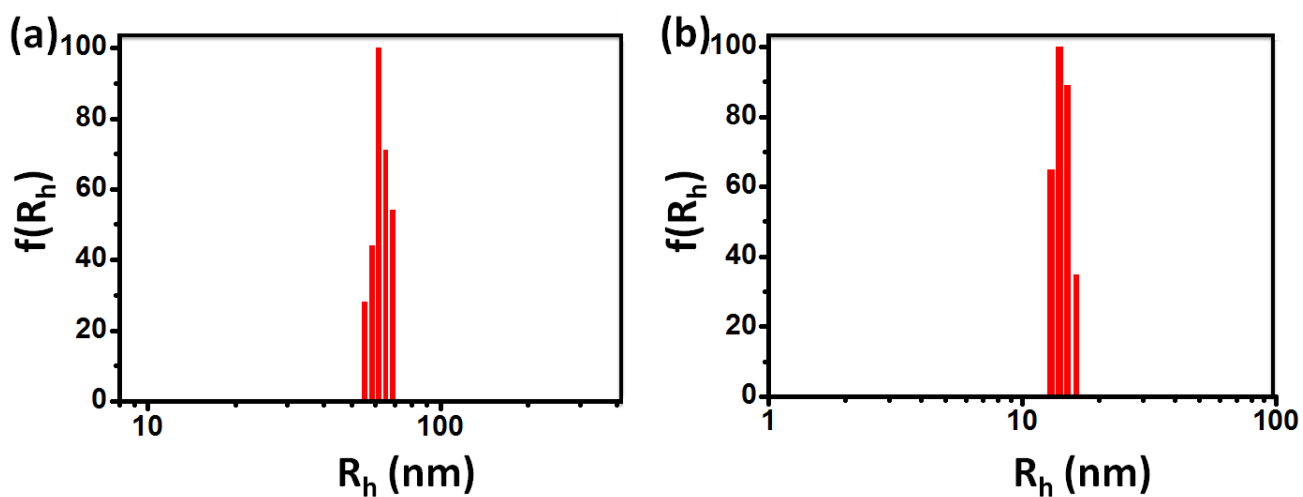


Fig. S10. DLS results for (a) vesicles, and (b) spheres of PS-(APOSS)₂-PS-1 micelles.

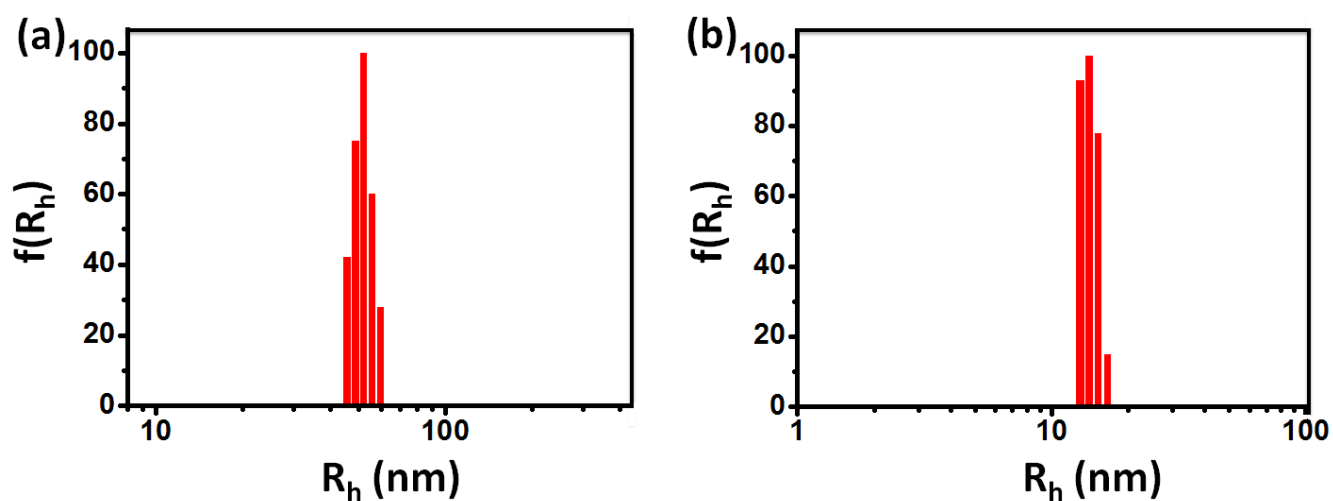


Fig. S11. DLS results for (a) vesicles, and (b) spheres of PS-(APOSS)₂-PS-2 micelles.

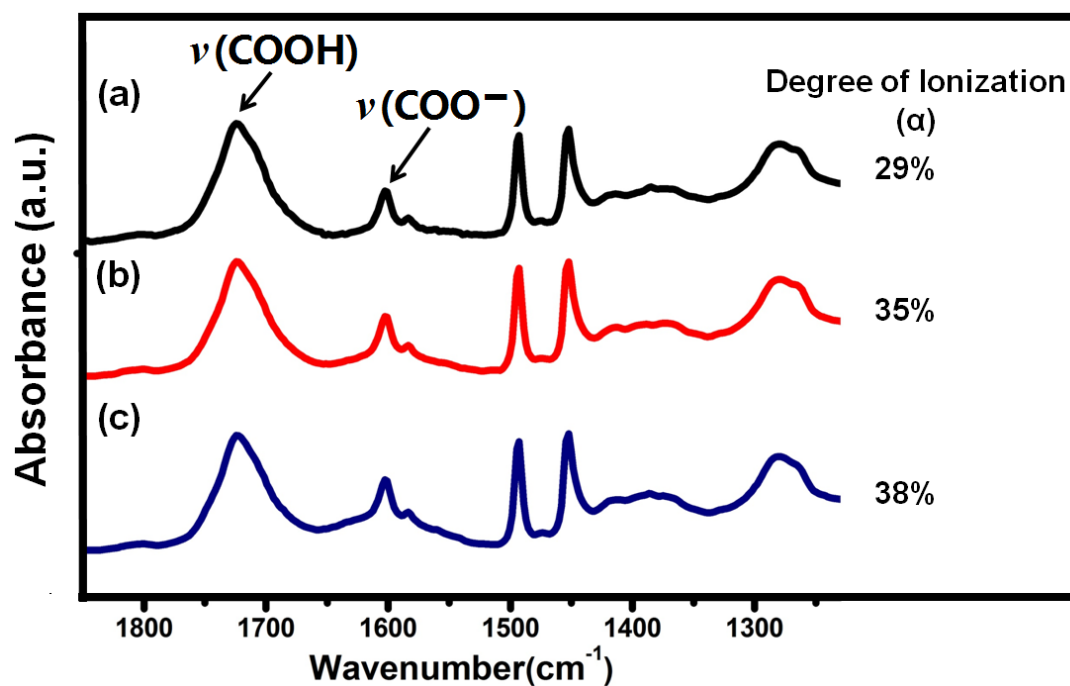


Fig. S12. FT-IR spectra of PS-(APOSS)₂-PS-1 freeze-dried from the micelle solutions in different common solvents: (a) 1,4-dioxane, (b) DMF, and (c) DMF/NaOH.

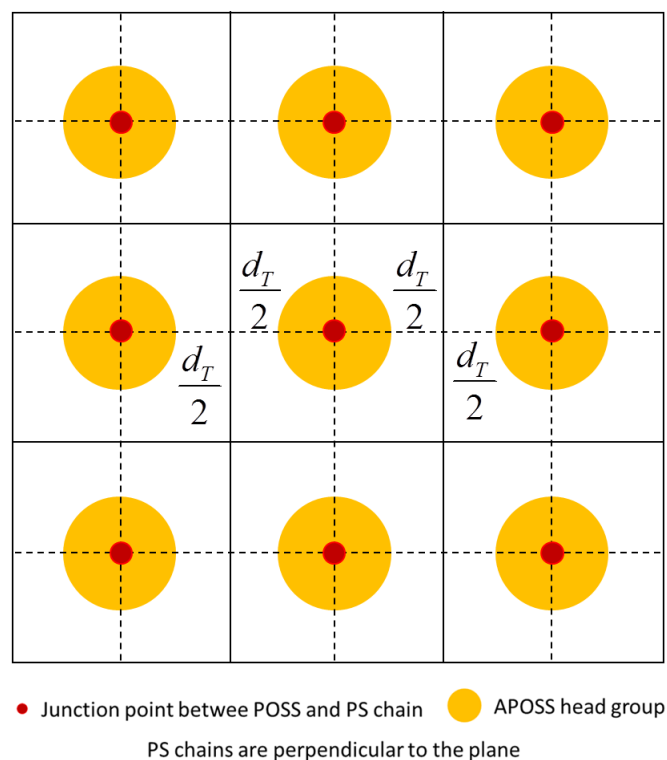


Fig. S13. Proposed model of giant surfactants packing on the micelle surface.

References:

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- S2 J. Choi and M. F. Rubner, *Macromolecules*, 2005, **38**, 116.