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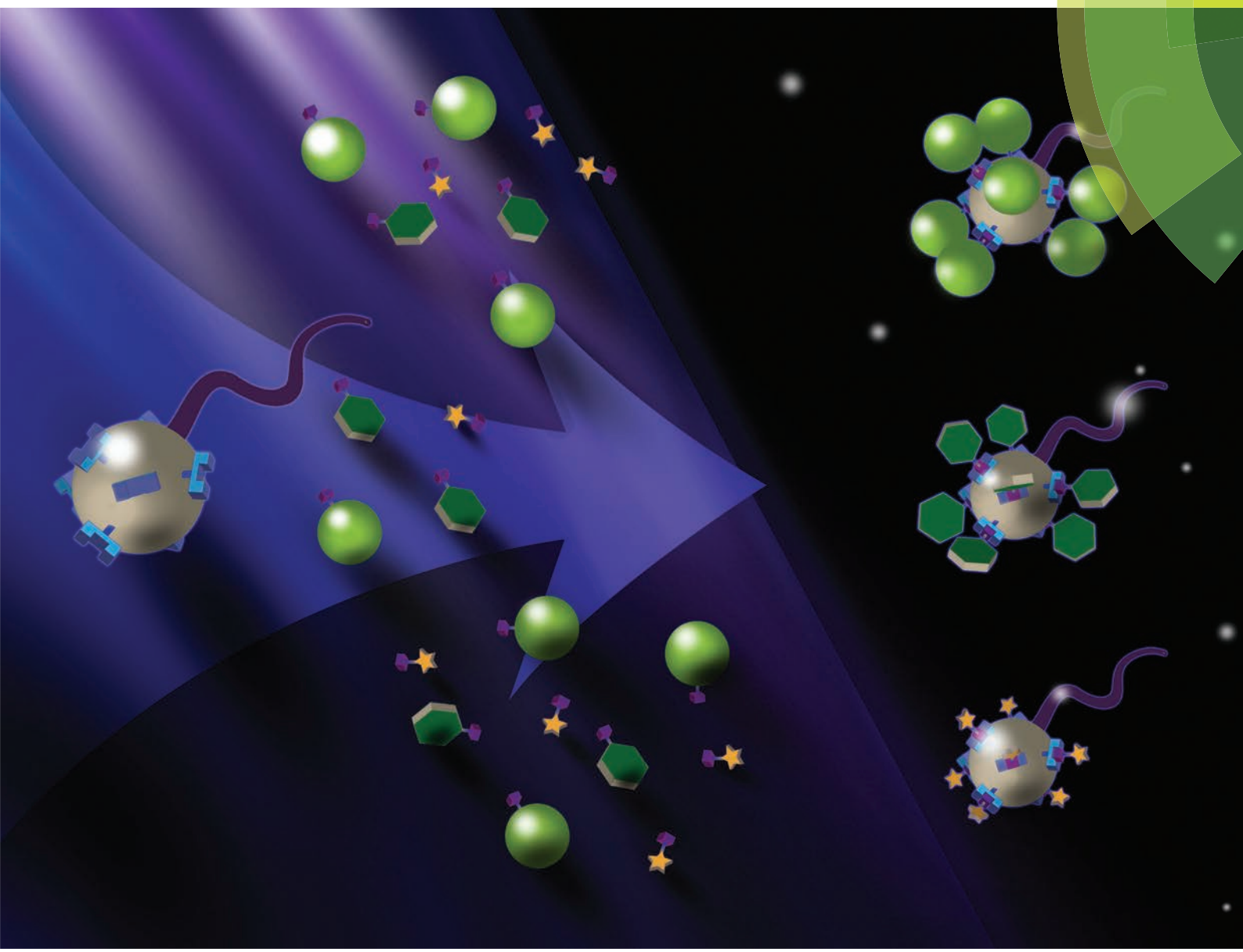

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Thiol-Michael "click" chemistry: another efficient tool for head functionalization of giant surfactants†

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One of the challenges in the precise synthesis of giant surfactants lies in the homogenous functionalization of a head with bulky ligands. In this article, we report the use of thiol-Michael "click" chemistry as a facile, modular and robust approach to address this issue. A giant surfactant with acryloxyl-functionalized POSS (ACPOSS) head was conveniently constructed from commercially available acrylo POSS and polystyrene (PS). Functional thiols with different sizes, such as 2-mercaptoethanol, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol, 1-thio-β-D-glucose tetraacetate (sugar-SH), and 2-naphthalenethiol, were attached onto the head of the ACPOSS-PS conjugate by thiol-Michael and thiol–ene reactions. It was found that while both the methods offer a straightforward and highly efficient approach to prepare uniform and precise giant surfactants with small thiol ligands, only the former proceeds without apparent side reactions when large and bulky thiols, such as sugar-SH and 2-naphthalenethiol, are used. The former method also eliminates the need for UV irradiation or heat initiation. Therefore, the mild condition, high efficiency, and broad functional group tolerance of thiol-Michael chemistry should further expand the scope of POSS-based giant surfactants with unparalleled possibilities for head surface chemistry manipulation, which provides numerous opportunities for nanofabrication by the direct self-assembly of giant surfactants.

Introduction

Progresses in materials science and macromolecular engineering rely heavily on self-assembling materials with well-defined, sophisticated architectures and tunable properties.[1–3] For example, the control over amino acid or nucleotides sequence that nature exerts on biopolymers leads to diverse structures and functions of different proteins or nucleic acids. Therefore, the design and synthesis of multi-functional macromolecules with precise structures is a prerequisite for future applications of advanced materials ranging from soft electronics to nanomedicine.[4–6]

Giant molecules are considered to be a new class of self-assembling materials in polymer science and macromolecular engineering.[7] This class of unique macromolecules are built upon molecular nanoparticle subunits or their conjugates with other nano-building blocks, and usually possess precisely-defined surface functionalities and well-controlled molecular architectures.[8,9] In particular, giant surfactants are regarded to be an important class of giant molecules and refer to polymer-tethered molecular nanoparticles.[7,10] Giant surfactants capture the essential structural features of small-molecule surfactants at overall sizes of several nanometers. Being a fascinating class of macromolecules from both structural and functional perspectives, they provide a versatile platform to engineer nanostructures with sub-10 nm feature sizes.[10,11] They bridge the gap between small-molecule surfactants and block copolymers with a duality of the self-assembly behaviors of both materials in solution and in the condensed state.[11]

In the past several years, functional polyhedral oligomeric silsesquioxane (POSS) nanoparticle–polymer conjugates became progressively important as model compounds for giant surfactants.[12,13] The precisely defined molecular structures and readily modifiable surface chemistry on POSS

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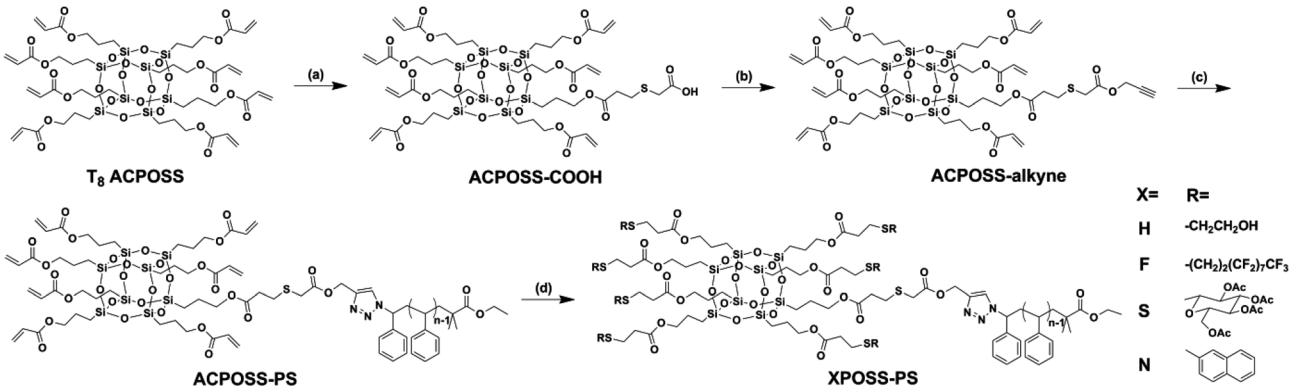

Scheme 1 Synthetic route for giant surfactants using sequential "click" chemistry: (a) 2-mercaptoacetic acid, triethylamine, THF, 25 °C, 29%; (b) propargyl alcohol, DPTS, DIPC, dry DMF, 0 °C, 81%; (c) PS_n-N_3, CuBr, PMDETA, toluene, 25 °C, 83%–91%; (d) Condition I (thiol-Michael reaction): R-SH, hexylamine, THF, 25 °C, 0.5–2 h, 81%–93%; Condition II (thiol–ene reaction): R-SH, DMPA, THF, 25 °C, 0.5–2 h, 84%–92%.

cage[14–20] allow the development of a library of giant surfactants in accordance to their small-molecule counterparts with various structural variations such as giant lipids,[21,22] giant bolaform surfactants,[23] symmetric and asymmetric giant gemini surfactants,[24,25] and multi-headed/multi-tailed giant surfactants.[23,26] Recently, the advent of "click" chemistry has led to an influx of new opportunities in the rational design and precise synthesis of POSS-based giant surfactants.[11,13,22,24–26] Several kinds of "click" reactions including Cu(I)-catalyzed [3 + 2] azide–alkyne cycloaddition (CuAAC),[13,24] strain-promoted azide–alkyne cycloaddition (SPAAC),[25,26] oxime ligation,[22,25] and thiol–ene addition[10–13] are among the most robust and reliable methods for POSS-polymer synthesis due to their remarkable efficiency and orthogonality. The development of general synthetic strategies based on their sequential[26] or orthogonal combination[22,25] are particularly exciting and facilitate the synthesis of highly complex macromolecular structures in more effective manners and fewer steps.[25]

The head functionalization of POSS in giant surfactants usually involves simultaneous, multi-site modification. High selectivity and efficiency are required to achieve complete reaction and circumvent the awfully difficult purification in removing side products or incompletely functionalized intermediates. Radical mediated thiol–ene addition has been demonstrated to be a very successful method in head surface chemistry diversification from a vinyl POSS precursor.[10,12,13] While thiol–ene chemistry[27–30] represents the general reaction between thiols and a broad scope of double bonds, we would like to reserve the term to describe only the radical-mediated addition of thiols across double bonds.[28,29] Thiol–ene reaction works well for small thiol ligands bearing functionalities such as hydroxyl groups,[12,21] carboxylic acid[12,26] and short alkyl chain.[13] However, sometimes, inhomogeneous products (such as dimers) occur when large and bulky thiol ligands are employed probably due to the radical recombination of intermediates.[12,31,32] The amount of side products may be reduced by using a large excess of thiols. However, it is a valid concern when high purity products with precise structures are desired,[32] especially for functional ligands that are useful in various applications but have relatively complex molecular structures and large sizes. We have been continuously seeking for alternative strategies to fulfill an even more general and effective head functionalization of POSS in giant surfactants.

In addition to thiol–ene chemistry, thiol-Michael reaction mediated by base or nucleophiles is a new type of "click" chemistry, as advocated by Hoyle,[28] Bowman[28] and Lowe.[29] Thiol-Michael reaction describes the base/nucleophile-mediated addition of a thiol group across activated double bonds.[33–40] It has attracted considerable attention as an important, highly reactive chemical ligation method under mild conditions and has prevalent applications in polymer chemistry and materials science, including polymer network and gel formation,[41,42] colloidal particles synthesis and surface engineering,[43,44] and star and branched polymers preparation.[45,46] We expect that the base/nucleophile-catalyzed hydrothiolation pathway of thiol-Michael reaction may circumvent the possibility of radical recombination, and hence be particularly suitable for POSS head functionalization with bulky ligand or UV-attenuating functional groups with minimum side products.[46–49] Thus, we performed a systematic study on the use of thiol-Michael "click" reaction for POSS head functionalization and compared the results to that of the thiol–ene "click" reaction (Scheme 1). Herein, we try to show that the thiol-Michael reaction is another powerful and versatile tool for POSS head surface diversification.

Experimental section

Chemicals and solvents

Styrene (Aldrich, 99%) was purified by distillation from calcium hydride under reduced pressure prior to use. Tetrahydrofuran (THF, Certified ACS, EM Science), methanol (Fisher Scientific, reagent grade), ethyl acetate (Fisher Scientific), toluene (Certified ACS), dichloromethane (Certified ACS), chloroform (Certified ACS), *N*,*N*-dimethylformamide (DMF, Aldrich, anhydrous 99.8%) and hexanes (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. 2-Mercaptoacetic acid (Aldrich, >98%) was distilled under reduced pressure before use. Acrylo POSS cage mixture (Hybrid Plastics, cage content >90%), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (Aldrich, 97%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylene-triamine (PMDETA, Aldrich, 99%), ethyl α-bromoisobutyrate (Aldrich, 98%), triethylamine (Aldrich, 99.5%), hexylamine (Aldrich, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99%), *N*,*N*′-diisopropylcarbodiimide (DIPC, Acros Organics, 99%), 4-(dimethylamino) pyridine (DMAP, Aldrich, 99%), sodium azide (Aldrich, >99%), 2-mercaptoethanol (Aldrich, >99%), 2-naphthalenethiol (Aldrich, 99%), 1-thio-β-D-glucose tetraacetate (sugar-SH, Alfa Aesar, 99%), and propargyl alcohol (Aldrich, 99%) were used as received. Silica gel (VWR, 230–400 mesh) was activated by heating at 140 °C for 12 h. Ultraviolet (UV) light irradiation of the samples was carried out with a 15 W UVP Black Ray UV bench lamp XX-15 L, emitting light with a wavelength of ~365 nm (intensity *ca.* 4.6 mW cm^{-2}). 4-(Dimethylamino) pyridinium toluene-*p*-sulfonate (DPTS)[24] and azido-end-capped polystyrene (PS_n-N_3)[24] were synthesized as reported.

Materials characterization

Size exclusion chromatographic (SEC) analyses for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10^3/10^4 Å), mixed bed (10^3, 10^4, 10^6 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 the eluent at a flow rate of 1.0 mL min^{-1} at 30 °C.

All ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ (Aldrich, 99.8% D) utilizing a Varian Mercury 500 NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton signals in $CDCl_3$ at δ 7.27 ppm; while the ^{13}C NMR spectra were referenced to $^{13}CDCl_3$ at δ 77.00 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 °C–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). The spectra were measured in positive reflectron 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, Aldrich, >98%) served as a matrix and was prepared in $CHCl_3$ at a concentration of 20 mg mL^{-1}. The cationizing agent sodium trifluoroacetate or silver trifluoroacetate was prepared in MeOH–$CHCl_3$ (v/v = 1/3) at a concentration of 5 mg mL^{-1} or 10 mg mL^{-1}. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All the samples were dissolved in $CHCl_3$ at a concentration of 10 mg mL^{-1}. 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/salt, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample (sandwich method). After solvent evaporation, the plate was inserted into the MALDI mass 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.

Synthetic procedures

T_8 ACPOSS. T_8 ACPOSS can be directly obtained by the chromatographic purification of 10 g commercial acrylo POSS (ACPOSS) cage mixture on silica gel with CH_2Cl_2–EtOAc (v/v = 20/3) (1421 mg, 14%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.35 (d, 1H, CH_aH$_b$═CH–), 6.10 (q, 1H, CH$_a$H$_b$═CH–), 5.79 (d, 1H, CH$_a$$H_b$═CH–), 4.10 (t, 2H, –C$H_2$OCO–), 1.75 (m, 2H, –SiCH$_2$CH_2–), 0.69 (t, 2H, –SiCH_2–). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 166.07, 130.49, 128.49, 66.09, 22.11, 8.00. MS (MALDI-TOF): Calcd for $C_{48}H_{72}NaO_{28}Si_8$ 1343.23, found: 1343.29 $(M{\cdot}Na)^+$.

ACPOSS-COOH. T_8 ACPOSS (500 mg, 0.379 mmol), 2-mercaptoacetic acid (35 mg, 0.379 mmol), and triethylamine (0.053 mL, 0.379 mmol) were dissolved in 100 mL of THF. After 30 min reaction, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with CH_2Cl_2–EtOAc (v/v = 2/1) as the eluent to afford the product as a colorless liquid (155 mg, 29%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 9.85 (s, 1H, *H*OOC–), 6.35 (d, 7H, CH_aH$_b$═CH–), 6.10 (q, 7H, CH$_a$H$_b$═CH–), 5.80 (d, 7H, CH$_a$$H_b$═CH–), 4.10 (t, 14H, –C$H_2$OCO–), 3.25 (s, 2H, –SC$H_2$COOH), 2.90 (t, 2H, –C$H_2SCH_2$COOH), 2.63 (t, 2H, –C$H_2CH_2$S–), 1.74 (m, 16H, –SiCH$_2CH_2$–), 0.68 (t, 16H, –SiC$H_2$–). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 173.49, 171.56, 166.11, 130.53, 128.44, 66.13, 34.19, 33.33, 27.48, 22.06, 7.96. MS (MALDI-TOF): Calcd *m*/*z* for $C_{50}H_{76}NaO_{30}SSi_8$ 1435.22, found: 1435.31 $(M{\cdot}Na)^+$; Calcd *m*/*z* for $C_{50}H_{75}Na_2O_{30}SSi_8$ 1457.20, found: 1457.32 $(M{\cdot}2Na - H)^+$.

ACPOSS-alkyne. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar was added ACPOSS-COOH (300 mg, 0.212 mmol), propargyl alcohol (13 mg, 0.233 mmol) and DPTS (63 mg, 0.212 mmol), followed by the addition of 20 mL freshly dried DMF 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 (40 mg, 0.318 mmol) was added dropwise *via* syringe. The mixture was allowed to warm up to room temperature and

stirred for another 12 h. The white precipitation was then filtered off and the filtrate was washed with water and brine, dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel with CH_2Cl_2–EtOAc (v/v = 20/3) as the eluent to afford the product (249 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, δ): 6.37 (d, 7H, CH_aH$_b$=CH–), 6.12 (q, 7H, CH$_a$H$_b$=CH–), 5.82 (d, 7H, CH$_a$$H_b$=CH–), 4.73 (d, 2H, –C$H_2$C≡CH), 4.10 (m, 16H, –C$H_2$OCO–), 3.28 (s, 2H, –SC$H_2$COO–), 2.92 (t, 2H, –C$H_2SCH_2$COO–), 2.65 (t, 2H, –C$H_2CH_2$S–), 2.50 (s, 1H, –CH$_2$C≡C$H$), 1.74 (m, 16H, –SiCH$_2CH_2$–), 0.68 (t, 16H, –SiC$H_2$–). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 171.45, 169.40, 166.06, 130.50, 128.49, 77.14, 75.35, 66.06, 52.69, 34.22, 33.29, 27.52, 22.11, 8.00. MS (MALDI-TOF): Calcd for $C_{53}H_{78}NaO_{30}SSi_8$ 1473.24, found: 1473.55 $(M{\cdot}Na)^+$.

General procedure for the synthesis of ACPOSS-PS$_n$ using CuAAC

To a 100 mL Schlenk flask equipped with a magnetic stirring bar was added ACPOSS-alkyne (1.0 equiv.), PS$_n$-N$_3$ (1.05 equiv.), CuBr (1 mg), and freshly distilled toluene. The resulting solution was degassed by three freeze–pump–thaw cycles before the addition of PMDETA *via* pipet. The mixture was then degassed again by one more cycle, and stirred at room temperature for another 24 h. 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 CH_2Cl_2–EtOAc (v/v = 1/1) was used to elute the product off the column. After solvent removal, the crude product was precipitated into cold MeOH. The product ACPOSS-PS$_n$ was collected and dried under vacuum overnight to give a white powder.

ACPOSS-PS$_{48}$. ACPOSS-alkyne (100 mg, 0.069 mmol), PS$_{48}$-N$_3$ (M_n = 5.1 kg mol^{-1}, 370 mg, 0.072 mmol), and CuBr (1 mg) were used. The product ACPOSS-PS$_{48}$ was collected and dried under vacuum overnight to afford a white powder (355 mg; yield: 83%). SEC: M_n = 6.2 kg mol^{-1}, PDI = 1.07.

ACPOSS-PS$_{76}$. ACPOSS-alkyne (100 mg, 0.069 mmol), PS$_{76}$-N$_3$ (M_n = 8.0 kg mol^{-1}, 576 mg, 0.072 mmol), and CuBr (1 mg) were used. The product ACPOSS-PS$_{76}$ was collected and dried under vacuum overnight to afford a white powder (534 mg; yield: 86%). SEC: M_n = 9.0 kg mol^{-1}, PDI = 1.02.

ACPOSS-PS$_{176}$. ACPOSS-alkyne (100 mg, 0.069 mmol), PS$_{176}$-N$_3$ (M_n = 18.4 kg mol^{-1}, 1325 mg, 0.072 mmol), and CuBr (1 mg) were used. The product ACPOSS-PS$_{176}$ was collected and dried under vacuum overnight to afford a white powder (1250 mg; yield: 91%). SEC: M_n = 19.9 kg mol^{-1}, PDI = 1.01.

General procedure for the synthesis of XPOSS-PS$_n$-TM using thiol-Michael "click" chemistry

ACPOSS-PS$_n$ (1.0 equiv.), functional thiol ligand (R-SH, 20.0 equiv.), and hexylamine (0.05 equiv.) were added to an open vial equipped with a magnetic stirring bar and dissolved in a minimum amount of THF solvent. The solution was stirred at room temperature for (0.5–2) h. After solvent removal, the crude product was purified by repeated precipitation. The product XPOSS-PS$_n$-TM was collected and dried under vacuum overnight to give a white powder.

HPOSS-PS$_{48}$-TM. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), 2-mercaptoethanol (26 mg, 322 μmol), and hexylamine (1 mg) were used. After 0.5 h reaction, the mixture was precipitated into cold methanol three times. The product was collected and dried under vacuum overnight to afford a white powder (88 mg; yield: 83%). SEC: M_n = 6.6 kg mol^{-1}, PDI = 1.06.

FPOSS-PS$_{48}$-TM. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (155 mg, 322 μmol), and hexylamine (1 mg) were used. After 1 h reaction, the mixture was precipitated into a cold mixture of methanol–hexanes (v/v = 5/1) three times. The product was collected and dried under vacuum overnight to afford a white powder (116 mg; yield: 85%). SEC: M_n = 8.5 kg mol^{-1}, PDI = 1.07.

SPOSS-PS$_{48}$-TM. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), sugar-SH (117 mg, 322 μmol), and hexylamine (1 mg) were used. After 2 h reaction, the mixture was precipitated into a cold mixture of methanol–hexanes (v/v = 5/1) three times. The product was collected and dried under vacuum overnight to afford a white powder (111 mg; yield: 81%). SEC: M_n = 8.5 kg mol^{-1}, PDI = 1.08.

NPOSS-PS$_{48}$-TM. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), 2-naphthalenethiol (52 mg, 322 μmol), and hexylamine (1 mg) were used. After 2 h reaction, the mixture was precipitated into a cold mixture of methanol–hexanes (v/v = 2/1) three times. The product was collected and dried under vacuum overnight to afford a white powder (118 mg; yield: 87%). SEC: M_n = 8.4 kg mol^{-1}, PDI = 1.05.

HPOSS-PS$_{76}$-TM. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), 2-mercaptoethanol (17 mg, 222 μmol), and hexylamine (1 mg) were used for 0.5 h reaction. After the same purification step as that of HPOSS-PS$_{48}$-TM, a white powder was obtained (90 mg; yield: 82%). SEC: M_n = 9.9 kg mol^{-1}, PDI = 1.06.

FPOSS-PS$_{76}$-TM. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (107 mg, 222 μmol), and hexylamine (1 mg) were used for 1 h reaction. After the same purification step as that of FPOSS-PS$_{48}$-TM, a white powder was obtained (99 mg; yield: 87%). SEC: M_n = 10.3 kg mol^{-1}, PDI = 1.04.

SPOSS-PS$_{76}$-TM. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), sugar-SH (81 mg, 222 μmol), and hexylamine (1 mg) were used for 2 h reaction. After the same purification step as that of SPOSS-PS$_{48}$-TM, a white powder was obtained (99 mg; yield: 86%). SEC: M_n = 10.4 kg mol^{-1}, PDI = 1.04.

NPOSS-PS$_{76}$-TM. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), 2-naphthalenethiol (36 mg, 222 μmol), and hexylamine (1 mg) were used for 2 h reaction. After the same purification step as that of NPOSS-PS$_{48}$-TM, a white powder was obtained (99 mg; yield: 89%). SEC: M_n = 10.0 kg mol^{-1}, PDI = 1.03.

HPOSS-PS$_{176}$-TM. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), 2-mercaptoethanol (8 mg, 100 μmol), and hexylamine (1 mg) were used for 0.5 h reaction. After the same purification step as that of HPOSS-PS$_{48}$-TM, a white powder was obtained (101 mg; yield: 88%). SEC: M_n = 22.5 kg mol^{-1}, PDI = 1.03.

FPOSS-PS$_{176}$-TM. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (48 mg, 100 μmol), and hexylamine (1 mg) were used for 1 h reaction. After the same purification step as that of FPOSS-PS$_{48}$-TM, a white powder was obtained (118 mg; yield: 91%). SEC: M_n = 23.5 kg mol^{-1}, PDI = 1.01.

SPOSS-PS$_{176}$-TM. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), sugar-SH (36 mg, 100 μmol), and hexylamine (1 mg) were used for 2 h reaction. After the same purification step as that of SPOSS-PS$_{48}$-TM, a white powder was obtained (121 mg; yield: 93%). SEC: M_n = 25.5 kg mol^{-1}, PDI = 1.01.

NPOSS-PS$_{176}$-TM. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), 2-naphthalenethiol (16 mg, 100 μmol), and hexylamine (1 mg) were used for 2 h reaction. After the same purification step as that of NPOSS-PS$_{48}$-TM, a white powder was obtained (109 mg; yield: 90%). SEC: M_n = 23.7 kg mol^{-1}, PDI = 1.04.

General procedure for the synthesis of XPOSS-PS$_n$-TE using thiol–ene "click" chemistry

ACPOSS-PS$_n$ (1.0 equiv.), functional thiol ligand (R-SH, 20.0 equiv.), and DMPA (0.05 equiv.) were added to an open vial equipped a magnetic stirring bar and dissolved in a minimum amount of THF solvent. The solution was irradiated under a 365 nm UV lamp at room temperature for (0.5–2) h. After solvent removal, the crude product was purified by repeated precipitation. The product XPOSS-PS$_n$-TE was collected and dried under vacuum overnight to give a white powder.

HPOSS-PS$_{48}$-TE. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), 2-mercaptoethanol (26 mg, 322 μmol), and DMPA (2 mg) were used for 0.5 h reaction with irradiation. After the same purification step as that of HPOSS-PS$_{48}$-TM, a white powder was obtained (89 mg; yield: 84%). SEC: M_n = 6.6 kg mol^{-1}, PDI = 1.06.

FPOSS-PS$_{48}$-TE. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (155 mg, 322 μmol), and DMPA (2 mg) were used for 1 h reaction with irradiation. After the same purification step as that of FPOSS-PS$_{48}$-TM, a white powder was obtained (116 mg; yield: 85%). SEC: M_n = 8.5 kg mol^{-1}, PDI = 1.06.

SPOSS-PS$_{48}$-TE. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), sugar-SH (117 mg, 322 μmol), and DMPA (2 mg) were used for 2 h reaction with irradiation. After the same purification step as that of SPOSS-PS$_{48}$-TM (116 mg; yield: 85%). SEC: M_n = 8.5 kg mol^{-1}, PDI = 1.16.

NPOSS-PS$_{48}$-TE. ACPOSS-PS$_{48}$ (M_n = 6.2 kg mol^{-1}, 100 mg, 16.1 μmol), 2-naphthalenethiol (52 mg, 322 μmol), and DMPA (2 mg) were used for 2 h reaction with irradiation. After the same purification step as that of NPOSS-PS$_{48}$-TM (119 mg; yield: 88%). SEC: M_n = 8.4 kg mol^{-1}, PDI = 1.17.

HPOSS-PS$_{76}$-TE. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), 2-mercaptoethanol (17 mg, 222 μmol), and DMPA (2 mg) were used for 0.5 h reaction with irradiation. After the same purification step as that of HPOSS-PS$_{48}$-TM, a white powder was obtained (93 mg; yield: 85%). SEC: M_n = 9.9 kg mol^{-1}, PDI = 1.08.

FPOSS-PS$_{76}$-TE. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (107 mg, 222 μmol), and DMPA (2 mg) were used for 1 h reaction with irradiation. After the same purification step as that of FPOSS-PS$_{48}$-TM, a white powder was obtained (99 mg; yield: 87%). SEC: M_n = 10.3 kg mol^{-1}, PDI = 1.04.

SPOSS-PS$_{76}$-TE. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), sugar-SH (81 mg, 222 μmol), and DMPA (2 mg) were used for 2 h reaction with irradiation. After the same purification step as that of SPOSS-PS$_{48}$-TM (99 mg; yield: 86%). SEC: M_n = 10.4 kg mol^{-1}, PDI = 1.19.

NPOSS-PS$_{76}$-TE. ACPOSS-PS$_{76}$ (M_n = 9.0 kg mol^{-1}, 100 mg, 11.1 μmol), 2-naphthalenethiol (36 mg, 222 μmol), and DMPA (2 mg) were used for 2 h reaction with irradiation. After the same purification step as that of NPOSS-PS$_{48}$-TM (99 mg; yield: 89%). SEC: M_n = 10.0 kg mol^{-1}, PDI = 1.14.

HPOSS-PS$_{176}$-TE. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), 2-mercaptoethanol (8 mg, 100 μmol), and DMPA (2 mg) were used for 0.5 h reaction with irradiation. After the same purification step as that of HPOSS-PS$_{48}$-TM, a white powder was obtained (100 mg; yield: 87%). SEC: M_n = 22.5 kg mol^{-1}, PDI = 1.02.

FPOSS-PS$_{176}$-TE. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (48 mg, 100 μmol), and DMPA (2 mg) were used for 1 h reaction with irradiation. After the same purification step as that of FPOSS-PS$_{48}$-TM, a white powder was obtained (109 mg; yield: 91%). SEC: M_n = 23.5 kg mol^{-1}, PDI = 1.10.

SPOSS-PS$_{176}$-TE. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), sugar-SH (36 mg, 100 μmol), and DMPA (2 mg) were used for 2 h reaction with irradiation. After the same purification step as that of SPOSS-PS$_{48}$-TM (116 mg; yield: 89%). SEC: M_n = 25.5 kg mol^{-1}, PDI = 1.13.

NPOSS-PS$_{176}$-TE. ACPOSS-PS$_{176}$ (M_n = 19.9 kg mol^{-1}, 100 mg, 5.1 μmol), 2-naphthalenethiol (16 mg, 100 μmol), and DMPA (2 mg) were used for 2 h reaction with irradiation. After the same purification step as that of NPOSS-PS$_{48}$-TM (111 mg; yield: 92%). SEC: M_n = 23.7 kg mol^{-1}, PDI = 1.18.

Results and discussion

POSS-based "clickable" building blocks with activated enes

Macromolecular precursors that contain activated enes on the POSS surface were designed and synthesized *via* CuAAC coupling reaction between azido-terminated polymer with different molecular weights and POSS-based mono-functional building blocks possessing seven acryloxyl groups and one alkyne group

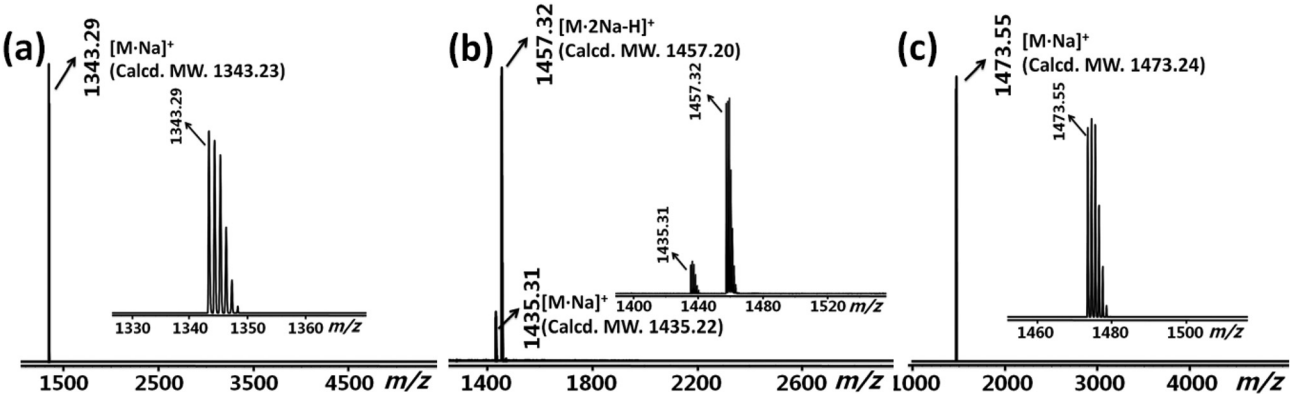

Fig. 1 MALDI-TOF mass spectra of (a) T_8 ACPOSS, (b) ACPOSS-COOH, and (c) ACPOSS-alkyne. The zoom-in view provided in the inset shows the related monoisotopic pattern for each sample.

(ACPOSS-alkyne). Four thiol ligands with different sizes (R-SH, *i.e.* 2-mercaptoethanol, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol, 1-thio-β-D-glucose tetraacetate (sugar-SH), and 2-naphthalenethiol) were then employed to functionalize the head using thiol-Michael and thiol–ene methods, respectively.

To evaluate and compare the efficiency of both these methods, a new "clickable" POSS with activated enes is required. T_8 Acrylo POSS (ACPOSS) is a suitable candidate since multiple acrylate groups on the POSS surface allow the facile chemical ligation with functional thiols *via* either thiol-Michael or thiol–ene "click" chemistry.[50] The T_8 ACPOSS can be directly isolated from commercial Acrylo POSS cage mixtures (Hybrid Plastics, cage content >90%) by flash chromatography in ~15% yield. The molecular structure and purity of the starting material are supported by the MALDI-TOF mass spectrum, where only one single peak matching the mass of the proposed structures is found. The mass peak at *m*/*z* 1343.29 shown in Fig. 1a perfectly agrees with the calculated monoisotopic molecular mass for T_8 ACPOSS ($C_{48}H_{72}NaO_{28}Si_8$ 1343.23 Da) and no other peaks corresponding to T_{10} or T_{12} products were observed.

The emergence of "click" chemistry offers a facile and versatile route to reduce the O_h symmetry of T_8 POSS cage to C_{3V} symmetry, generating a variety of monofunctional POSS-based "clickable" building blocks.[51] In this study, the monofunctionalization reaction was performed by simply mixing equimolar amounts of a functional thiol (2-mercaptoacetic acid) and T_8 ACPOSS in the presence of triethylamine (catalyst for thiol-Michael reaction)[35] at room temperature for ~30 min. Similar to thiol–ene monoadducts reported previously,[51] the monofunctional product, ACPOSS-COOH, can be purified by flash chromatography in a comparable yield (~30%). Both experimental observations from NMR and MALDI-TOF mass spectrometry (Fig. 1b) confirm the successful thiol-Michael synthesis of ACPOSS-COOH.

Considering the ready availability of azido-terminated polymer (PS_n-N_3) with different chain lengths, a versatile "clickable" building block, ACPOSS-alkyne (Scheme 1), was designed and synthesized for further construction of giant surfactant precursors with activated enes. The reaction was performed with a stoichiometric mixture of ACPOSS-COOH and propargyl alcohol in the presence of 4-(dimethylamino) pyridinium toluene-*p*-sulfonate (DPTS) and *N*,*N*′-diisopropylcarbodiimide (DIPC) in dry DMF. The colorless liquid-like product can then be purified by flash chromatography in a good yield (81%). The successful incorporation of the alkyne group is demonstrated by the characteristic proton (l) resonance at δ 2.50 ppm in the ^{1}H NMR spectrum (Fig. S1a†) and related resonances of alkyne carbons (m, n) at δ 77.14 and 75.35 ppm in the ^{13}C NMR spectrum (Fig. S1b†). The MALDI-TOF mass spectrum (Fig. 1c) also displays a single peak at *m*/*z* 1473.55 that agrees well with the calculated monoisotopic molecular mass for ACPOSS-alkyne (1473.24 Da). All the results demonstrate the successful esterification and the high purity of the product. ACPOSS-alkyne contains two kinds of "click" functionalities: an alkyne group for CuAAC conjugation with polymer tails, and seven acryloxyl groups for further head surface modifications *via* thiol-Michael/thiol–ene "click" chemistry.

Synthesis of ACPOSS-PS conjugate

Although normal vinyl groups on POSS cages are known to be inert under CuAAC reaction,[13] the compatibility between acryloxyl groups (activated enes) and CuAAC remains unknown. It was firstly examined by using low molecular weight azido-terminated polymer (PS_{48}-N_3, M_n = 5.1 kg mol^{-1}, PDI = 1.02) and ACPOSS-alkyne under a typical CuAAC condition (Scheme 1). The resulting product, ACPOSS-PS_{48}, is fully characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, SEC and MALDI-TOF mass spectrometry. In the FT-IR spectrum of Fig. S2,† the disappearance of the strong characteristic vibrational band for the azide group at 2090 cm^{-1} indicates the successful consumption of PS_{48}-N_3.[13] This is also proven by the complete absence of alkyne proton (l) in the ^{1}H NMR spectrum (Fig. 2a) after the CuAAC reaction. In addition, the intact acryloxyl groups on the POSS surface are directly confirmed by the two resonance signals at δ 6.23 and δ 5.88 ppm in the ^{1}H NMR spectrum (Fig. 2a) and two characteristic peaks at δ 130.65 and

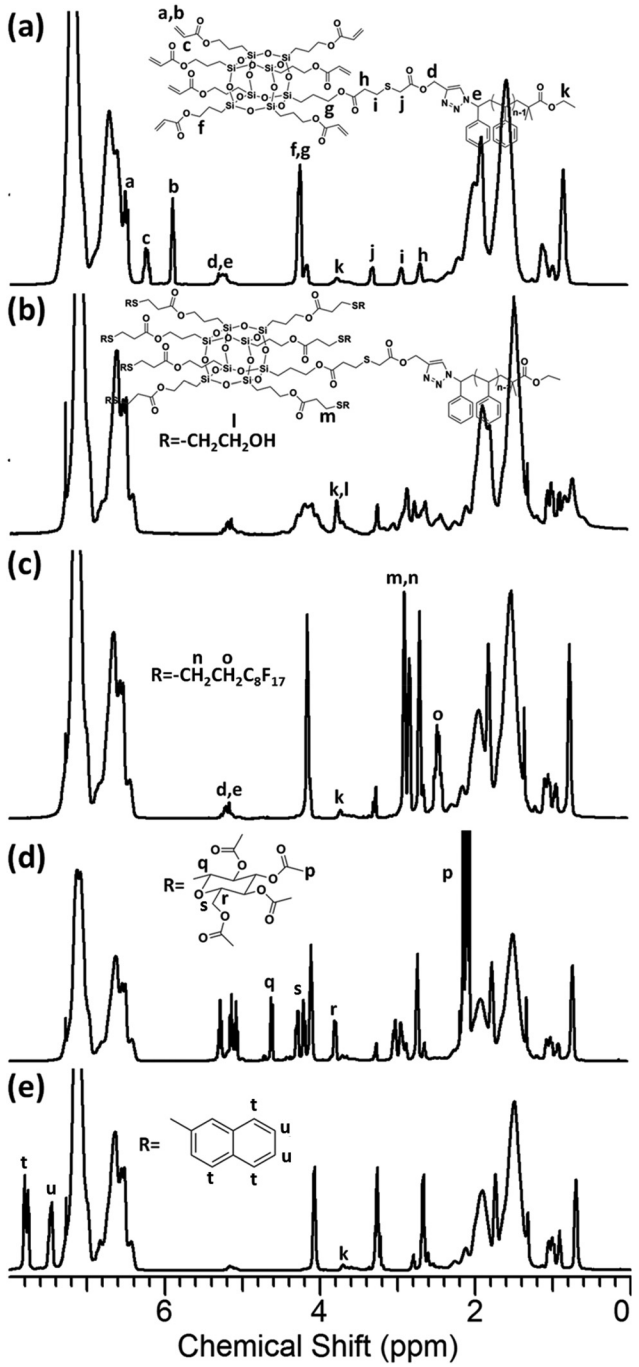

Fig. 2 ^{1}H NMR spectra of (a) ACPOSS-PS_{48}, (b) HPOSS-PS_{48}-TM, (c) FPOSS-PS_{48}-TM, (d) SPOSS-PS_{48}-TM, and (e) NPOSS-PS_{48}-TM.

δ 128.60 ppm in the ^{13}C NMR spectrum (Fig. S3a†). However, the proton on the newly formed triazole ring cannot be distinguished. It may overlap with the peaks of the aromatic protons of the PS block. Moreover, the SEC overlay (Fig. 3a) reveals a decreased retention volume of ACPOSS-PS_{48} relative to PS_{48}-N_3, which is consistent with the increased molecular weight and a larger hydrodynamic volume of the giant surfactant precursor (M_n = 6.2 kg mol^{-1}, PDI = 1.07, Table 1). The most striking evidence comes from the MALDI-TOF mass spectrum, as shown in Fig. 3b. Only one single symmetric distribution of molecular weights was observed under the positive reflectron mode, where the monoisotopic mass of each peak matches perfectly with that expected for the proposed structure (*e.g.*, for 38-mer with the formula of $C_{363}H_{393}N_3NaO_{32}SSi_8$, observed *m*/*z* 5584.69 Da *vs.* Calcd 5584.70 Da). All of the above evidence confirms the macromolecular structure and purity of ACPOSS-PS_{48}.

Similarly, two additional giant surfactant precursors with different chain lengths (ACPOSS-PS_{76} and ACPOSS-PS_{176}) were also synthesized *via* the CuAAC coupling reaction between ACPOSS-alkyne with PS_{76}-N_3 (M_n = 8.0 kg mol^{-1}, PDI = 1.03) and PS_{176}-N_3 (M_n = 18.4 kg mol^{-1}, PDI = 1.02), respectively. In Fig. 3c, the SEC overlay shows a single symmetric distribution for ACPOSS-PS_{76} (M_n = 9.0 kg mol^{-1}, PDI = 1.02, Table 1) shifted to a slightly lower retention volume relative to that of PS_{76}-N_3 due to a smaller increase in the molecular weight. A similar SEC result for ACPOSS-PS_{176} (M_n = 19.9 kg mol^{-1}, PDI = 1.01, Table 1) is shown in Fig. 3d. Therefore, it can be concluded that the three ACPOSS-PS conjugates with different PS tails have been successfully prepared, which are model compounds for further head surface functionalization using either thiol-Michael or thiol–ene "click" chemistry.

Head functionalization *via* thiol-Michael/thiol–ene chemistry

To examine the efficiency for the head surface functionalization of giant surfactants, three ACPOSS-PS_n conjugates with different PS tail lengths were employed as the macromolecular precursors to react with functional thiols of various sizes using thiol-Michael and thiol–ene "click" reactions. The thiols include 2-mercaptoethanol as a typical small thiol, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol as a medium one, and sugar-SH and 2-naphthalenethiol as model bulky thiol ligands. The head functionalization was performed using exactly the same stoichiometry, concentration, and reaction time. The thiol-Michael functionalization strategy was performed by mixing ACPOSS-PS_n (1.0 equiv.), R-SH (20.0 equiv.), and hexylamine (catalyst, 0.05 equiv.) in a minimum amount of common solvent (such as $CHCl_3$ or THF). The solution was then stirred at room temperature for about (0.5–2) h to finish the reaction. No chromatographic purification was involved in the purification process, and the excess thiol and remaining catalysts were conveniently removed by repeated precipitations. Most of the experimental conditions were identical for the thiol–ene functionalization, except that DMPA was used as the photo-initiator and that the reaction was irradiated under a 365 nm UV lamp at room temperature. Ideally, the products obtained by either method should be identical. To distinguish them and reveal the effect of the functionalization method, we use "XPOSS-PS_n-TM" and "XPOSS-PS_n-TE" to represent the samples prepared by thiol-Michael reaction and thiol–ene reaction, respectively.

As the model small-sized functional thiol, 2-mercaptoethanol was employed to evaluate the feasibility and versatility of thiol-Michael and thiol–ene "click" chemistries for the head

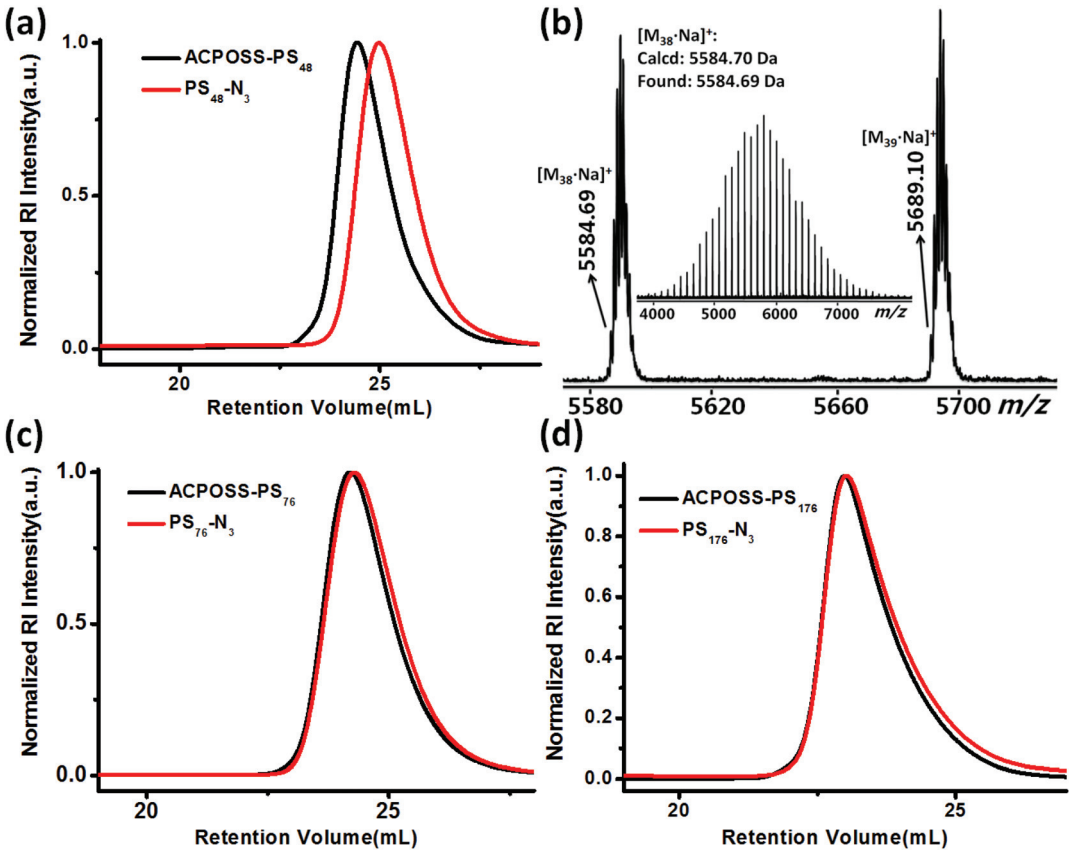

Fig. 3 (a) SEC overlay of ACPOSS-PS_{48} (black curve) and PS_{48}-N_3 (red curve); (b) MALDI-TOF mass spectrum of ACPOSS-PS_{48} (The result was obtained in positive reflectron mode with isotopic distribution. The inset shows the corresponding full spectrum); (c) SEC overlay of ACPOSS-PS_{76} (black curve) and PS_{76}-N_3 (red curve); (d) SEC overlay of ACPOSS-PS_{176} (black curve) and PS_{176}-N_3 (red curve).

functionalizations of the giant surfactants. After the thiol-Michael reaction between ACPOSS-PS_{48} and 2-mercaptoethanol, the macromolecular structures and uniformity of the resulting product, HPOSS-PS_{48}-TM, was fully demonstrated by various characterizations including ^{1}H NMR (Fig. 2b), ^{13}C NMR (Fig. S3b†), FT-IR (Fig. S2†), SEC (Fig. 4a) and MALDI-TOF mass spectrometry (Fig. 5a). Compared with the NMR spectrum of ACPOSS-PS_{48}, the disappearance of acryloxyl protons in the resonance peaks at δ 6.23 and δ 5.88 ppm in the ^{1}H NMR spectrum (Fig. 2b) and sp^2 carbon signals at δ 130.65 and δ 128.60 ppm (Fig. S3b†) in the ^{13}C NMR spectrum of HPOSS-PS_{48} confirms the complete thiol-Michael functionalization of the ACPOSS cage. It agrees with the new strong characteristic vibrational band at around 3300 cm^{-1} corresponding to the installed multiple hydroxyl groups in the FT-IR spectrum (Fig. S2†). The homogeneity of the thiol-Michael product can be demonstrated by the observation of a single symmetric peak (M_n = 6.6 kg mol^{-1}, PDI = 1.06) in the SEC overlay (Fig. 4a) and the single narrow molecular weight distribution in the MALDI-TOF mass spectrum (Fig. 5a). Specifically, the latter one was obtained under the positive linear mode due to the relatively high molecular weight of HPOSS-PS_{48}. Although high resolution isotopic distribution is not possible in this molecular weight range, the average molecular weights of the peaks match well with the calculated values (*e.g.*, for 40-mer with a sodium ion, observed *m*/*z* 6344.98 Da *vs.* Calcd 6344.68 Da). All these molecular characterizations above clearly prove the success of the thiol-Michael model reaction for ACPOSS-PS_{48}. Similar functionalization was also successful in ACPOSS-PS_{76} and ACPOSS-PS_{176} to afford the desired homogenous amphiphilic macromolecules, which are directly confirmed by NMR (Fig. S4 and S5†) and SEC results (Fig. 4b and 4c).

In our previous study, thiol–ene chemistry was usually employed to modify the periphery vinyl groups of VPOSS–polymer with various thiols, such as 2-mercaptoethanol,[21,22] 1-thioglycerol,[11,12] and 2-mercaptoacetic acid.[10,12] The head surface functionalization of ACPOSS-PS_n using 2-mercaptoethanol *via* the thiol–ene reaction was also smooth and straightforward. The successful preparation of three HPOSS-PS_n-TE samples was unambiguously supported by ^{1}H NMR (Fig. S4, S5 and S6†) and SEC chromatogram (Fig. 4a–4c). Therefore, it could be concluded that both thiol-Michael and thiol–ene chemistries are highly efficient and precise approaches to introduce 2-mercaptoethanol onto the POSS surface, which can also be applied to many other small thiols with various functionalities for fine-tuning of the interaction parameters in giant surfactants.

Table 1 Summary of molecular characterizations of polymers

Sample	$M_{n,\ SEC}$ (g mol^{-1})	$M_{w,\ SEC}$ (g mol^{-1})	PDI	High MW shoulder on SEC trace	Note
PS_{48}-N_3	5.1k	5.2k	1.02	No	Fig. 3a
ACPOSS-PS_{48}	6.2k	6.6k	1.07	No	Fig. 3a
HPOSS-PS_{48}-TM	6.6k	7.0k	1.06	No	Fig. 4a
HPOSS-PS_{48}-TE	6.6k	7.0k	1.06	No	Fig. 4a
FPOSS-PS_{48}-TM	8.5k	9.1k	1.07	No	Fig. 4d
FPOSS-PS_{48}-TE	8.5k	9.0k	1.06	No	Fig. 4d
SPOSS-PS_{48}-TM	8.5k	9.2k	1.08	No	Fig. 4g
SPOSS-PS_{48}-TE	8.5k	9.9k	1.16	Yes	Fig. 4g
NPOSS-PS_{48}-TM	8.4k	8.8k	1.05	No	Fig. 4j
NPOSS-PS_{48}-TE	8.4k	9.8k	1.17	Yes	Fig. 4j
PS_{76}-N_3	8.0k	8.2k	1.03	No	Fig. 3c
ACPOSS-PS_{76}	9.0k	9.2k	1.02	No	Fig. 3c
HPOSS-PS_{76}-TM	9.9k	10.5k	1.06	No	Fig. 4b
HPOSS-PS_{76}-TE	9.9k	10.7k	1.08	No	Fig. 4b
FPOSS-PS_{76}-TM	10.3k	10.7k	1.04	No	Fig. 4e
FPOSS-PS_{76}-TE	10.3k	10.7k	1.04	No	Fig. 4e
SPOSS-PS_{76}-TM	10.4k	10.8k	1.04	No	Fig. 4h
SPOSS-PS_{76}-TE	10.4k	12.4k	1.19	Yes	Fig. 4h
NPOSS-PS_{76}-TM	10.0k	10.3k	1.03	No	Fig. 4k
NPOSS-PS_{76}-TE	10.0k	11.4k	1.14	Yes	Fig. 4k
PS_{176}-N_3	18.4k	18.7k	1.02	No	Fig. 3d
ACPOSS-PS_{176}	19.9k	20.1k	1.01	No	Fig. 3d
HPOSS-PS_{176}-TM	22.5k	23.2k	1.03	No	Fig. 4c
HPOSS-PS_{176}-TE	22.5k	23.0k	1.02	No	Fig. 4c
FPOSS-PS_{176}-TM	23.5k	23.7k	1.01	No	Fig. 4f
FPOSS-PS_{176}-TE	23.5k	25.9k	1.10	Yes	Fig. 4f
SPOSS-PS_{176}-TM	25.5k	25.8k	1.01	No	Fig. 4i
SPOSS-PS_{176}-TE	25.5k	28.8k	1.13	Yes	Fig. 4i
NPOSS-PS_{176}-TM	23.7k	24.6k	1.04	No	Fig. 4l
NPOSS-PS_{176}-TE	23.7k	28.0k	1.18	Yes	Fig. 4l

Fluorinated POSS (FPOSS)-based giant surfactants have attracted remarkable attention due to their unique properties in numerous practical applications and hierarchical supramolecular engineering.[11,31,32] Whilst many synthetic efforts have been well documented, a facile and robust route towards precisely defined FPOSS-containing giant surfactants remains a grand challenge.[32] Undesired side reactions (such as radical coupling) were occasionally observed during the simultaneous multi-site functionalization of POSS head in VPOSS–polymer conjugates when commercial fluoroalkyl thiols (*i.e.* 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol) are used.[31] The situation is worse for the precursors with high molecular weight or for preparing targets with high fluoro-contents.[32] In this study, both thiol-Michael and thiol–ene "click" reactions were used to incorporate 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (as a model medium-sized thiol compound) onto the ACPOSS-PS_n head surface to generate FPOSS-based giant surfactants (FPOSS-PS_n-TM or -TE) with different tail lengths. The final products were fully characterized to check the efficiency and feasibility of these two approaches.

The successful thiol-Michael fluorination of ACPOSS-PS_{48} was confirmed by the complete disappearance of acryloxyl proton and unsaturated carbon resonances in the ^{1}H NMR spectrum (Fig. 2c) and ^{13}C NMR spectrum (Fig. S3c†), respectively. The most striking structural evidence comes from the MALDI-TOF mass spectrometry in Fig. 5b. Despite the relatively high molecular weight of FPOSS-PS_{48}-TM, a clean MALDI-TOF mass spectrum was still obtained where only one single distribution could be found. Although excellent isotopic resolution is not possible in this molecular weight range, the average molecular weights of the peaks match well with the calculated value. The SEC result in Fig. 4d also attests to the homogeneity of the resulting product by showing a single narrow symmetric peak (M_n = 8.5 kg mol^{-1}, PDI = 1.07, Table 1). Moreover, the thiol-Michael reaction continues to be successful for the fluorination of the POSS head of giant surfactants with even longer chains. The evidence of the NMR spectrum (Fig. S7a and S8a†) and SEC overlays (Fig. 4e and 4f) has also unambiguously proven the precise ligation process and the homogeneity of the fluorous giant surfactant (FPOSS-PS_{76}-TM and FPOSS-PS_{176}-TM).

The fluorination of the POSS head surface *via* a thiol–ene reaction also works well for the precursors of ACPOSS tethered with relatively short PS chains (ACPOSS-PS_{48} and ACPOSS-PS_{76}), which was directly supported by the NMR (Fig. S9 and S7b†) and SEC results (Fig. 4d and 4e). However, it was found that the thiol–ene reaction between 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol and ACPOSS-PS_{176} was complicated by the formation of a high molecular weight shoulder as observed by the small bump on the SEC trace (Fig. 4f). A similar phenomenon has been observed previously in VPOSS–polymer systems and has been attributed to the dimer formation by radical recombination.[31] The thiol-Michael reaction is perhaps advantageous for achieving a homogenous functionalization

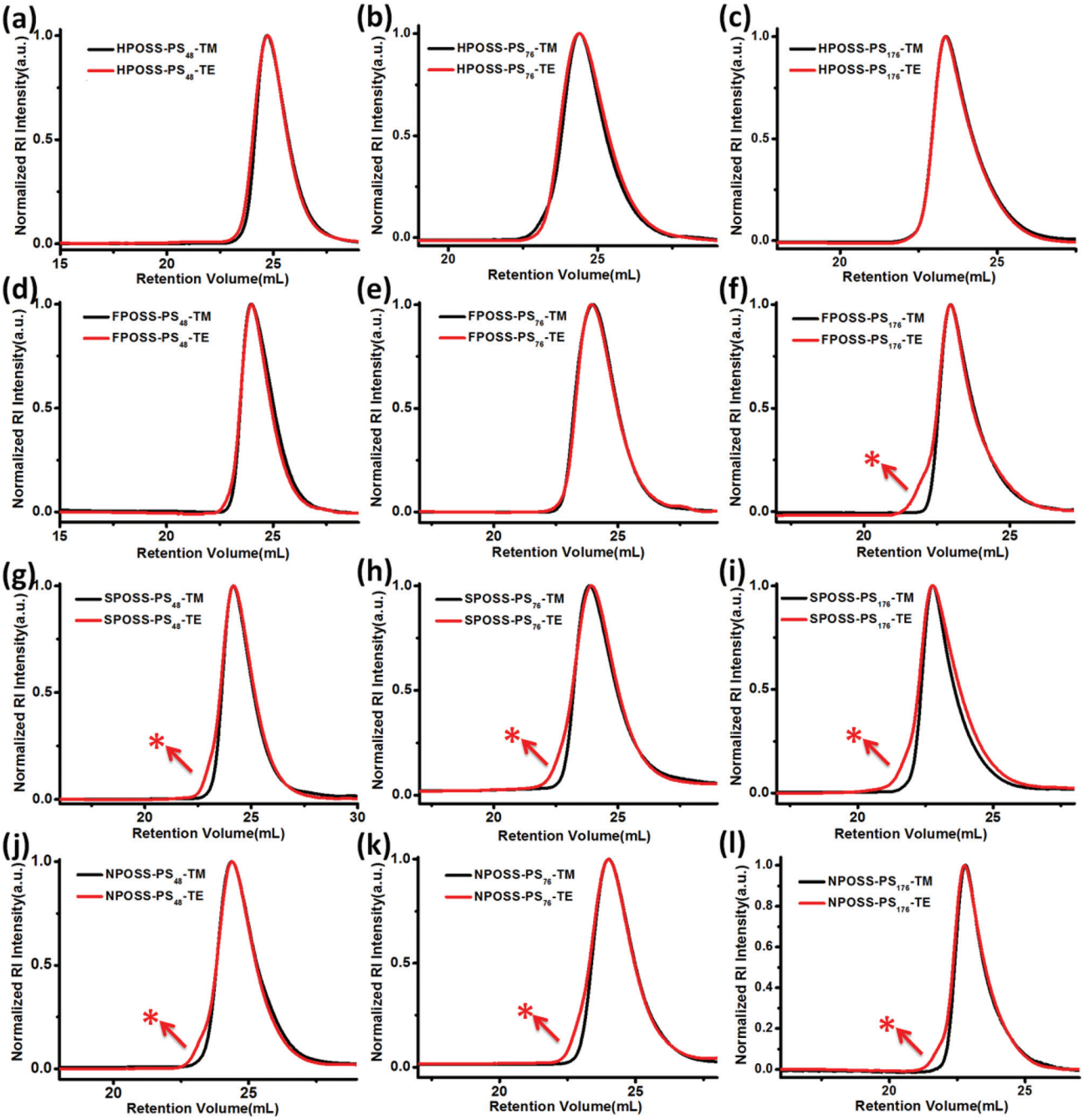

Fig. 4 SEC overlays for polymers. The black curves represent the products obtained by the thiol-Michael reaction, while the red curves represent the products obtained by the thiol–ene reaction (* indicates the small shoulder shown in the SEC curve).

in high molecular weight samples where chain entanglement and excluded volume effect on the reaction efficiency cannot be ignored.

Finally, two kinds of bulky model thiol compounds, sugar-SH and 2-naphthalenethiol, were also applied to evaluate the feasibility of the thiol-Michael and thiol–ene chemistries for the head modifications of the macromolecular precursors with different tail lengths. Again, the success of thiol-Michael head functionalization strategy is fully supported by the evidence from ^{1}H NMR (Fig. 2d, 2e, S10a, S11a, S12a, and S13a†), ^{13}C NMR (Fig. S3d and S3e†), FT-IR (Fig. S14†), SEC (Fig. 4g–4i and 4j–4l), and MALDI-TOF mass spectrometry (Fig. 5c and 5d) for both SPOSS-PS$_n$-TM and NPOSS-PS$_n$-TM series of samples. In particular, both of the SEC overlays (Fig. 4) and MALDI-TOF mass spectrometry (Fig. 5c and 5d) could directly validate the structural homogeneity and purity of the targeted products by the observation of symmetric signal peaks in the spectra. In contrast, while the thiol–ene reaction is also able to effectively transform all the activated enes into desired functionalities (see ^{1}H NMR results in Fig. S10b, S11b, S12b, S13b,

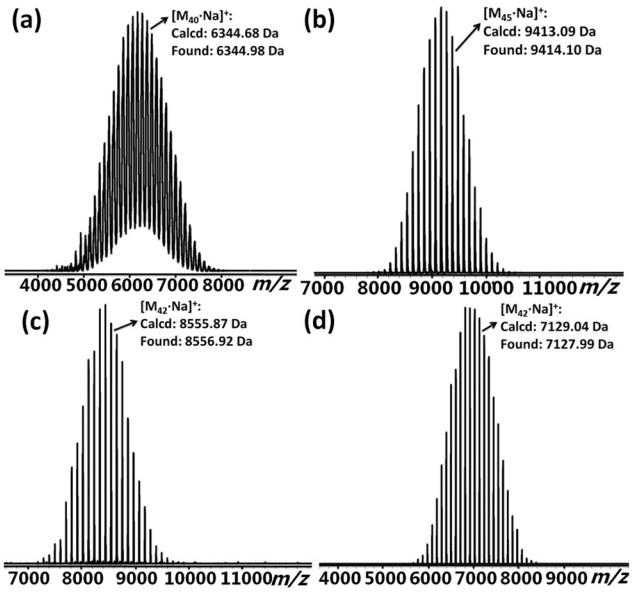

Fig. 5 MALDI-TOF mass spectra of (a) HPOSS-PS_{48}-TM, (b) FPOSS-PS_{48}-TM, (c) SPOSS-PS_{48}-TM, and (d) NPOSS-PS_{48}-TM. The full spectrum was obtained in the positive linear mode.

S15 and S16†), it also leads to the formation of an undesired high molecular weight fraction as revealed by the small bump on the SEC trace in Fig. 4g–4i and Fig. 4j–4l.[12] Although the formation of side products might be minimized by using an excess of R-SH, it cannot be completely avoided when the thiols are bulky.[12] In addition, for the typical thiol–acrylate system, radical mediated thiol–ene reaction would possibly involve the homopolymerization of acrylates, which might sometimes induce much more complex inhomogeneous byproducts during the reaction.[28,29] Therefore, to achieve a more precise control of macromolecular uniformity *via* thiol–ene chemistry, an alternative "pre-head functionalization" strategy has to be used to construct the target materials.[32] In comparison, the thiol-Michael chemistry is advantageous for the head modifications of giant surfactants with relatively bulky thiols, such as sugar-SH and 2-naphthalenethiol.

Conclusions

In summary, we have successfully applied the thiol-Michael reaction to the head functionalization of giant surfactants. The method was found to be a highly efficient and convenient way to introduce functionalities of various sizes onto the ACPOSS surface of giant surfactant precursors in a modular way. Although the thiol–ene reaction has proven successful in the synthesis of giant surfactants, the thiol-Michael reaction is found to be more versatile and powerful and possesses special advantages for samples with high MW tails or with bulky thiol ligands. This study could offer numerous opportunities to further construct novel POSS-based macromolecules from ACPOSS-PS, such as giant surfactants possessing a patchy head (using thiol-functionalized nanoparticles) and miktoarm star polymers (using thiol-functionalized polymers *via* RAFT polymerization). Work is ongoing in our group to develop the new generation of POSS-based giant surfactants in which the heads are coated with various optics,[52,53] energy[54] and therapeutics[55]-related functionalities *via* the thiol-Michael "click" reaction, which shall underline the practical usage of these well-defined soft hybrid materials.

Acknowledgements

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