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Sequential "Click" Synthesis of "Nano-Diamond-Ring-like" Giant Surfactants Based on Functionalized Hydrophilic POSS/C_{60} Tethered with Cyclic Polystyrenes

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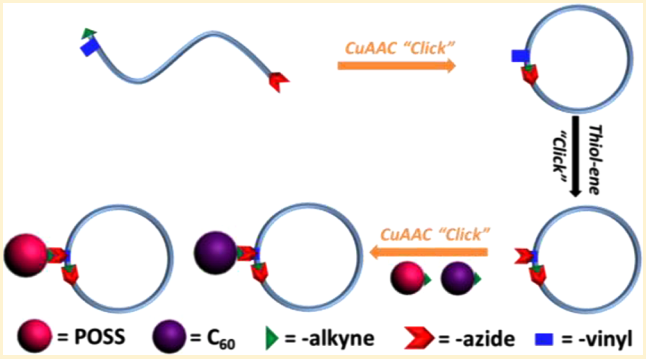
Supporting Information

ABSTRACT: This paper reports the design and facile synthesis of a novel series of "nano-diamond-ring-like" giant surfactants composed of a functionalized hydrophilic polyhedral oligomeric silsesquioxane (such as dihydroxyl-functionalized DPOSS) or fullerene (such as carboxylic acid-functionalized AC_{60}) head as the "diamond" and a hydrophobic, cyclic polystyrene (CPS) tail as the "ring". The synthetic route combines several steps of "click-type" reactions, demonstrating highly efficient and modular features. Starting from a specifically designed initiator, trifunctional linear polystyrene (LPS) precursors bearing vinyl, bromo, and alkyne groups were prepared by atom transfer radical polymerization (ATRP). Upon the subsequent azidation of LPS, copper-catalyzed Huisgen [3 + 2] cycloaddition reaction was employed to afford vinyl-functionalized CPS ring in high yield and purity. The vinyl group was then subjected to the thiol−ene reaction to introduce an azide group onto the CPS, providing an azide-functionalized CPS (CPS-N_3) as a "clickable" cyclic building block to construct giant molecules. Various "nano-diamond-ring-like" giant surfactants decorating with different "diamonds", such as hydrophilic DPOSS or AC_{60} molecular nanoparticles, can be readily synthesized via the modular sequential "click" approaches based on this CPS-N_3 building block. These giant surfactants with structural precision represent a novel member in the MNP-based giant surfactant family which might have distinct self-assembly behaviors compared to their linear analogues.



INTRODUCTION

Over the past decade, we have witnessed explosive efforts in studying self-assembly[1−3] of fundamental building blocks (typically atoms, molecules, macromolecules, and colloid particles) to construct various nanostructures, which serves as the basis for the alternative "bottom-up" approach toward manufacturing nanomaterials with unique properties.[1−6] Creating hierarchical self-assembled nanostructures with molecular-level precision beyond those from traditional amphiphilic moieties[7−9] remains to be one major challenge in material sciences.[10−12] The emergence of "giant molecules" based on "nanoatoms" provides new opportunities to achieve this goal.[13] Using molecular nanoparticles (MNPs) as the "nanoatoms" (or basic nanosized building blocks), giant molecules with precisely defined structures can be obtained by conjugating MNPs with other nanobuilding blocks.[13] Specifically, giant surfactants,[14−16] composed of MNPs tethered by polymer tails, are one of the representative prototype giant molecules. Giant surfactants capture the essential structural features of small-molecule surfactants but possess amplified sizes which are comparable to block copolymer amphiphiles.[14] Because of the use of sequential "click-type" reactions[17−23] in the synthetic approaches, chemical structures and properties of giant surfactants can be tuned by separately changing the chemical compositions[24−27] and molecular architectures[27−29] of

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the MNP heads and the polymer tails, in a modular and systematic manner.[13]

Our group has been developing a library of MNPs with precisely defined chemical structures and surface functionalities for the construction of giant surfactants, among which polyhedral oligomeric silsesquioxane (POSS)[30−33] and [60] fullerene (C_{60})[34−36] derivatives are the most promising candidates. POSS and C_{60} are cagelike molecules with persistent three-dimensional conformations and monodisperse size around 1 nm. At the periphery of the silicon−oxygen cubic backbones of the POSS molecules[31−33] and the truncated icosahedral framework of C_{60} moieties,[36,37] different functional groups can be introduced by well-established elegant chemistry, resulting in a set of homo- or heterofunctionalized POSS[26,38,39] and C_{60} derivatives[27,35] as versatile functionalized building blocks.

Giant surfactants deriving from POSS/C_{60}-based "nanoatoms" have demonstrated rich and unique self-assembly behaviors in solution, thin film, and the bulk states.[14−16,27] For example, giant surfactants constructed from a hydrophilic C_{60} (carboxylic acid-functionalized AC_{60}) head and polystyrene (PS) tails can form different micellar and colloidal particle morphologies in solution, depending on the selection of common solvent, initial molar concentration, and the length of the PS tails.[14,27] More interestingly, comparison between two sets of topological isomers indicates that their self-assembly is extremely sensitive to the molecular architecture. Giant surfactants constructed by a hydrophilic C_{60} (AC_{60}) tethered with one long or two short PS chains (AC_{60}-PS_{44} or AC_{60}-$2PS_{23}$), both of which possess comparable overall molecular weights, exhibit considerably different self-assembled morphologies in the bulk and solution.[14,27] Similar architectural influence on self-assembled structures has also been displayed in dihydroxyl-functionalized POSS−PS systems.[14] These distinct differences in self-assembly behaviors between the topological isomers drive us to further investigate the molecular architecture effect.

Cyclic polymers are known to possess a variety of unique properties that are distinguishable from their linear analogues, including effects relating to no chain ends, reduced overall dimension, lower viscosity, and increased glass transition temperature (T_g).[40] As a result, a substantial body of work[41−43] has been devoted to efficient preparation of cyclic homopolymers[44−54] or cyclic block copolymers[55−59] as well as to their physical characterizations. Recently, the development of a few highly efficient cyclization methods utilizing, for example, the copper-catalyzed alkyne−azide Huisgen [3 + 2] cycloaddition reaction,[44] the Diels−Alder reaction,[54] or even the genetically encoded SpyTag−SpyCatcher chemistry,[60] has greatly facilitated the preparation of various cyclic polymers and the study on their physical properties. For example, gels formed from cyclic poly(5-hydroxy-1-cyclooctene) (PACOE) exhibit notably greater swelling ability and larger strain at break than those from linear PACOEs;[50] thermal stabilities of micelles are greatly enhanced through a linear-to-cyclic conversion of triblock amphiphilic copolymer;[55] smaller ordered domains in thin film are achieved from cyclic polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) block copolymers than those from the linear counterparts;[57] tadpole-shaped linear−cyclic (c-PNIPAM)-*b*-PCL block copolymers exhibit improved drug loading and releasing capacity compared with linear amphiphilic diblock PNIPAM-*b*-PCL copolymers,[59] among many others. These inspiring results further drive us to use cyclic polymers as the building blocks to design and construct MNP-based giant surfactants and to investigate their self-assembling behaviors. To the best of our knowledge, there is no report on the synthesis of giant surfactants on the basis of cyclic polymer-tethered MNPs.

In this article, we strive to introduce a new member to the family of giant surfactants based on "nanoatoms". The molecular design is to tether a cyclic hydrophobic PS chain onto a hydrophilic POSS/C_{60} head, which can be viewed as "nano-diamond-ring-like" giant surfactants. To achieve an efficient, facile, and modular synthetic approach, we design a synthetic approach that combines several steps of highly efficient reactions, which fulfills the "click" criteria. First, we use the CuAAC reaction[17,18,44] in the cyclization step[44] to synthesize a cyclic PS with a vinyl group (Vinyl-CPS), which can be converted to an azide group via the thiol−ene reaction.[19,20,22] The azide monofunctionalized CPS building block (CPS-N_3) is then compatible with the reported sequential "click" strategy[26] toward POSS/C_{60}-based giant surfactants. The developed synthetic route is highly efficient, and all of the important intermediates and final products have been well characterized. Moreover, the CPS-N_3 might serve as a versatile building block and can be easily applied to afford other giant surfactants. These "nano-diamond-ring-like" giant surfactants prepared and reported here possess distinctive and unique molecular structures and are excellent targets to investigate the structure−property relationships in our giant surfactant systems.

EXPERIMENTAL SECTION

Chemicals and Solvents. Methanol (reagent grade, Fisher Scientific), chloroform (Certified ACS, Fisher Scientific), dichloromethane (DCM, Fisher Scientific), ethyl acetate (EA, Fisher Scientific), tetrahydrofuran (THF, Fisher Scientific), *N*,*N*-dimethylformamide (DMF, anhydrous 99.8%, Sigma-Aldrich), and hexanes (Certified ACS, Fisher Scientific) were used as received. Toluene (ACS grade, EMD) and styrene (99%, Sigma-Aldrich) were used after purification in a manner reported previously.[35] Anhydrous sodium sulfate (Na_2SO_4), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-Aldrich), copper(I) bromide (98%, Acros Organics), 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, 98%, Sigma-Aldrich), 1-thioglycerol (≥98%, Fluka), trifluoroacetic acid (99%, Sigma-Aldrich), sodium azide (NaN_3, 99.5%, Sigma-Aldrich), [60]fullerene (C_{60}, MTR Ltd., 99.5%), and octavinyl-POSS (OVPOSS, >97%, Hybrid Plastics) were used as received. The functionalized POSS derivative containing seven vinyl groups and one alkyne group (VPOSS-alkyne)[26] and C_{60} derivative installing ten protected carboxylic acid groups and one alkyne group (TC_{60}-alkyne)[27] were prepared according to our previous publications.

Characterization. All ^{1}H NMR and ^{13}C NMR spectra were collected using a Varian Mercury 300 or Varian NMRS 500-01 spectrometer. NMR samples were prepared with concentration of 10−20 mg/mL in $CDCl_3$ or DMSO-d_6 for ^{1}H NMR or 50−80 mg/mL for ^{13}C NMR. The ^{1}H NMR spectra were referenced to δ 7.27 ppm in $CDCl_3$ or δ 2.50 ppm in DMSO-d_6, and ^{13}C NMR spectra were referenced to δ 77.00 ppm in $CDCl_3$ or δ 39.43 ppm in DMSO-d_6. For VPOSS-CPS or TC_{60}-CPS, the integration ratio between the characteristic vinyl peaks on POSS at δ 6.20−5.84 ppm (21H per VPOSS) or characteristic peaks on C_{60} at δ 4.89−4.47 ppm (20H per TC_{60}) and the peaks at δ 7.45−6.35 ppm (aromatic protons in PS) gives the number-average degree of polymerization (DP) of the PS. The calcuated molecular weight ($M_{n,NMR}$) can then be obtained by the summation of $M_{n,PS}$ (DP × 104.1 g/mol), $M_{iniator}$ (323.1 g/mol), $M_{2\text{-azidoethanethiol}}$ (103.0 g/mol), and $M_{POSS/C60}$ (730.0 g/mol for VPOSS, 1486.1 g/mol for DPOSS, 2552.7 g/mol for TC_{60}, and 1991.9 g/mol for AC_{60}). In DOSY experiments, the samples were

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dissolved in $CDCl_3$ to make a solution of 15 mg/mL in NMR tube with a height of 5 cm. Measurements were performed at 25 °C on a Varian NMRS 500 spectrometer. An interval of 100 ms between the gradient pulse and 1 ms duration of gradient pulse was applied. The gradient strength was varied in 32 gradient steps within a range from 0.1 to 10 T/m.

Infrared spectra were collected on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA). Samples were prepared by depositing polymer solution with concentration of about 10 mg/mL in THF onto a KBr plate, followed by drying with blowing air at room temperature to give drop-casting films. The data were analyzed using the Win-IR software.

Size-exclusion chromatography (SEC) analyses were carried out 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 double detector system, which is consisted of a differential refractometer (Waters 410) and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as the eluent with a flow rate of 1.0 mL/min at 30 °C and as the solvent to prepare sample solutions with the concentration of ca. 5−10 mg/mL. The sample solutions were filtered through a 0.45 μm Teflon filter prior to injection. Regular SEC calibrations were conducted based on PS standards (Polymer Laboratories).

Matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billarica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. Positive reflection or linear mode was applied to measure all of spectra. Calibration with external PS standards was required before each measurement. *trans*-2-(3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) was served as matrix (20 mg/mL in $CHCl_3$) and sodium trifluoroacetate (NaTFA) was used as the cationizing agent (10 mg/mL in methanol). Both of them were mixed in the ratio of 10/1 (v/v). In sample preparation, 0.5 μL of the matrix/NaTFA mixture was deposited on microtiter plate wells (MTP 384-well ground steel plate), followed by depositing 0.5 μL of sample solution (ca. 10 mg/mL in THF) on the top of a dry matrix/NaTFA spot and adding another 0.5 μL of the matrix/NaTFA mixture. After evaporation of solvent, the target plate was loaded for data collection. Data analysis was performed with the Bruker's flexAnalysis software.

LPS-Br. Compound **2** (200 mg, 0.557 mmol, 1 equiv), CuBr (80.2 mg, 0.557 mmol, 1 equiv), styrene (11.6 g, 0.11 mol, 200 equiv), and freshly distilled toluene (8 mL) were added into a 100 mL Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze−pump−thaw cycles, followed by adding PMDETA (96.4 mg, 0.557 mmol, 1 equiv) under nitrogen protection. After one further freeze−pump−thaw cycle, the flask was immersed into a 110 °C oil bath. The reaction was quenched in liquid nitrogen after a prescribed time. Then the crude mixture was directly transferred onto a short silica gel column to remove copper salts, and THF was used to elute the product. The concentrated mixture was precipitated into the methanol, collected by vacuum filtration, and dried *in vacuo* to afford the product as a white powder. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.21−6.31 (br, 140H), 5.85 (s, 1H), 5,19 (m, 2H), 5.05 (m, 2H), 4.45 (m, 2H), 3.96 (m, 2H), 3.43 (m, 2H), 2.53−2.43 (m, 4H), 2.31−1.24 (br, 84H), 0.92 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 176.7, 170.7, 145.4, 134.6, 128.7−125.3, 117.3, 82.3, 72.2, 70.5, 69.1, 68.3, 62.2, 46.3−39.6, 33.3, 26.7, 14.4. FT-IR (KBr) ν (cm^{-1}): 3303, 3082, 3060, 3026, 2924, 2851, 1942, 1735, 1601, 1493, 1452, 1367, 1154, 1128, 1068, 1028, 907, 758, 698, 539. $M_{n,NMR}$ = 3.3 kg/mol. SEC results: $M_{n,SEC}$ = 3.3 kg/mol, $M_{w,SEC}$ = 3.4 kg/mol, $Đ$ = 1.04.

LPS-N$_3$. Sodium azide (0.26 g, 4 mmol, 10 equiv) was added into a solution of LPS-Br ($M_{n,NMR}$ = 3.3 kg/mol, $Đ$ = 1.04, 1.5 g, 0.4 mmol, 1 equiv) in DMF. The mixture was stirred at room temperature for 48 h. The resultant mixture was diluted with 200 mL of CH_2Cl_2 and washed with water for three times to remove unreacted salts. After concentrating the organic fraction, the mixture was precipitated into a cold methanol, followed by filtrating and drying *in vacuo* to afford the polymer product (1.3 g) as a white powder. Yield: 87%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.26−6.31 (br, 140H), 5.85 (m, 1H), 5,20 (m, 2H), 5.04 (m, 2H), 4.45 (m, 2H), 3.96 (m, 2H), 3.42 (m, 2H), 2.58−2.43 (m, 4H), 2.33−1.26 (br, 84H), 0.91 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 176.7, 170.7, 145.4, 134.6, 128.7−125.3, 117.3, 82.3, 72.2, 70.5, 69.1, 68.3, 62.2, 46.3−39.6, 33.3, 26.7, 14.4. FT-IR (KBr) ν (cm^{-1}): 3297, 3082, 3055, 3018, 2924, 2832, 2095, 1946, 1732, 1601, 1489, 1443, 1367, 1154, 1128, 1070, 902, 752, 687, 539. $M_{n,NMR}$ = 3.3 kg/mol. SEC results: $M_{n,SEC}$ = 3.3 kg/mol, $M_{w,SEC}$ = 3.4 kg/mol, $Đ$ = 1.05.

Vinyl-CPS. To a 2 L round-bottomed flask equipped with a magnetic stirrer, CuBr (500 mg) and freshly dried toluene (1 L) were added and bubbled with nitrogen for 24 h. Then, PMDETA (500 mg) was injected into the above mixture via gastight syringe. LPS-N_3 ($M_{n,NMR}$ = 3.3 kg/mol, $Đ$ = 1.05, 300 mg, 0.09 mmol) was dissolved in 20 mL of freshly dried toluene and degassed by three freeze−pump−thaw cycles, followed by slowly injecting into the round-bottomed flask in 48 h at 50 °C via a syringe pump. After completing injection, the reaction was carried out for another 24 h. After removal of solvent, the crude mixture was transferred directly onto a short column of silica gel, which was first eluted by mixing solvent of toluene/hexane (v/v = 3/1) to remove any unreacted LPS precursor. The fraction containing Vinyl-CPS was obtained by using a mixture solvent of toluene/EA (v/v = 2/1) as eluent. After removal of solvent, the residues were precipitated into cold methanol. Vinyl-CPS (240 mg) was afforded by filtration and drying *in vacuo* as a white powder. Yield: 80%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.38−6.31 (m, 140H), 5.83 (m, 1H), 5,19 (m, 2H), 5.04 (m, 2H), 3.93 (m, 2H), 3.40 (m, 2H), 2.93 (m, 2H), 2.64 (m, 2H), 2.41−1.17 (br, 84H), 0.93 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 175.7, 170.6, 144.6, 133.4, 127.8−124.1, 116.2, 71.1, 70.5, 69.5, 67.2, 61.4, 45.2−40.4, 39.5, 28.7, 19.0, 8.2. FT-IR (KBr) ν (cm^{-1}): 3082, 3064, 3018, 2915, 2841, 1946, 1741, 1601, 1489, 1442, 1023, 902, 172, 696, 538. $M_{n,NMR}$ = 3.3 kg/mol. SEC results: $M_{n,SEC}$ = 3.1 kg/mol, $M_{w,SEC}$ = 3.3 kg/mol, $Đ$ = 1.07.

CPS-N$_3$. Vinyl-CPS ($M_{n,NMR}$ = 3.3 kg/mol, $Đ$ = 1.07, 200 mg, 0.06 mmol, 1 equiv), 2-azidoethanethiol (20 mg, 0.18 mmol, 3 equiv), and photoinitiator Irgacure 2959 (2 mg, 0.009 mmol, 0.15 equiv) were dissolved in 2 mL of THF, followed by irradiation with UV (365 nm) for 30 min. The solution was then precipitated in the cold methanol twice and collected by filtration. The white dried product was given after drying in vacuum oven overnight. Yield: 76%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.26−6.44 (m, br, 140H), 5.02 (m, 2H), 3.94 (m, 2H), 3.44 (m, 4H), 2.94 (m, 2H), 2.82−2.53 (m, 6H), 2.45−1.25 (m, br, 86H), 0.94 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 172.1, 170.6, 145.8, 129.2−125.1, 70.3, 69.7,69.3, 65.3, 62.2, 51.2, 46.8−39.6, 31.5, 29.6, 29.0 21.1. FT-IR (KBr) ν (cm^{-1}): 3083, 3064, 3027, 2924, 2850, 2095, 1946, 1741, 1601, 1489, 1442, 1023, 892, 752, 696, 528. $M_{n,NMR}$ = 3.4 kg/mol. SEC results $M_{n,SEC}$ = 3.1 kg/mol, $M_{w,SEC}$ = 3.3 kg/mol, $Đ$ = 1.06.

VPOSS-CPS. CPS-N_3 ($M_{n,NMR}$ = 3.4 kg/mol, $Đ$ = 1.06, 150 mg, 0.045 mmol, 1 equiv), CuBr (1 mg, 0.007 mol, 0.15 equiv), VPOSS-alkyne (36 mg, 0.049 mmol, 1.1 equiv), and freshly distilled toluene (10 mL) were added into a 100 mL Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze−pump−thaw cycles, followed by introducing PMDETA (8 mg, 0.045 mmol, 1 equiv) under nitrogen protection. After one further freeze−pump−thaw cycle, the reaction was carried out for 16 h at room temperature. Then the crude mixture was directly applied onto a short column filled with a silica gel. CH_2Cl_2 was first used as eluent to remove excessive VPOSS-alkyne, and then the mixing solvent of CH_2Cl_2/EA (v/v = 4/1) was used to give resulting fraction. After removal of solvent, the mixture was precipitated in the methanol, collected by vacuum filtration, and dried *in vacuo* to afford the product as a white powder (149 mg). Yield: 82%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.34−6.42 (m, br, 140H), 6.16−5.89 (m, 21H), 5.00 (m, 2H), 4.44 (m, 2H), 4.25 (m, 2H), 3.39 (m, 4H), 3.02−2.94 (m, 4H), 2.92−2.54 (m, 8H), 2.45−1.52 (m, br, 86H), 1.21 (m, 2H), 0.92 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 173.3, 145.6, 137.6, 130.2−126.1, 122.2, 69.2, 68.0, 61.2, 50.2, 47.6−38.9, 33.7, 32.0, 30.3, 29.6, 28.7, 27.4, 22.6, 20.9, 13.1. FT-IR (KBr) ν (cm^{-1}): 3083, 3064, 3027, 2924, 2850, 1732, 1601, 1498, 1442, 1120 (Si−O−Si, asymmetric stretching), 892, 762,

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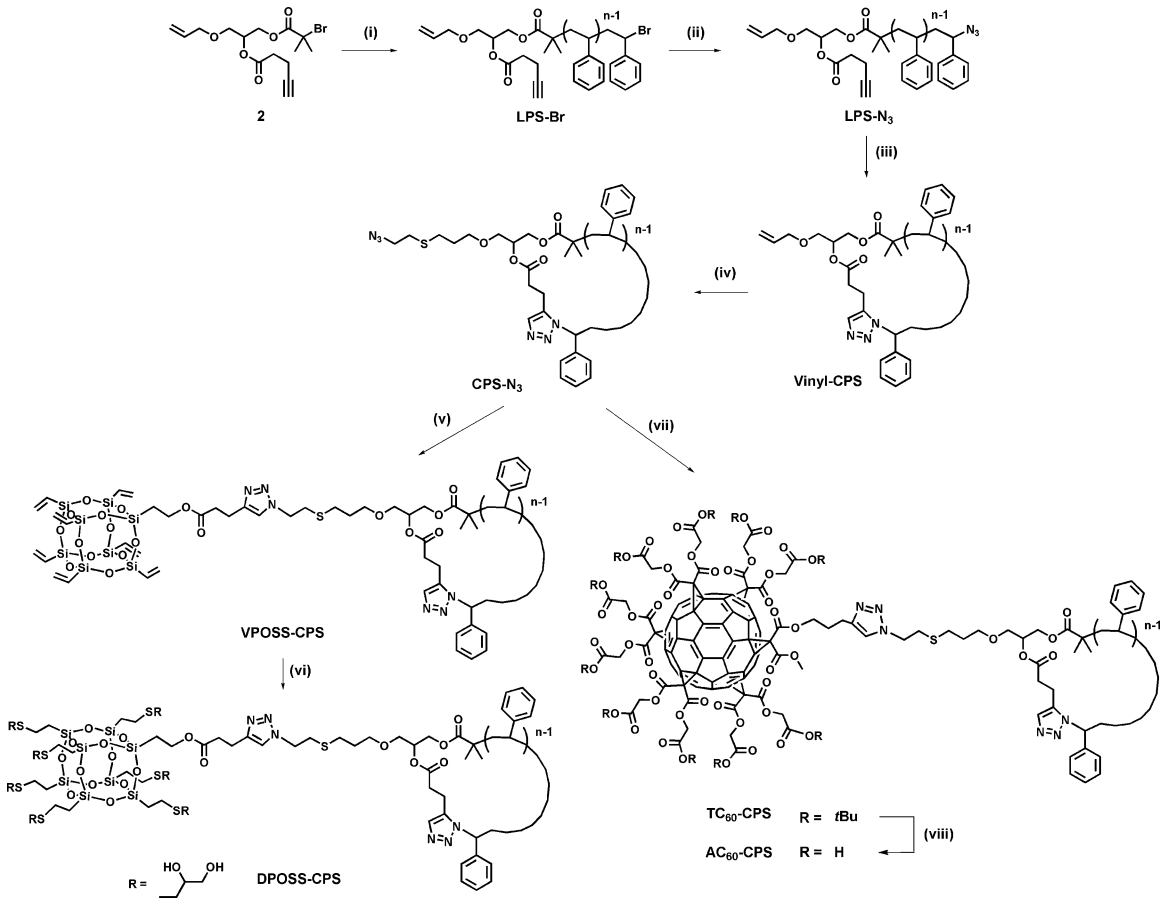
Scheme 1. Synthesis of DPOSS-CPS and AC_{60}-CPS[a]



[a]Reagents and conditions: (i) styrene, CuBr, PMDETA, toluene, 110 °C, 20%; (ii) NaN_3, DMF, room temperature (rt), 87%; (iii) CuBr, PMDETA, toluene, rt, 80%; (iv) $N_3CH_2CH_2SH$, Irgacure 2959, THF, *hv*, 30 min, rt, 76%; (v) VPOSS-alkyne, CuBr, PMDETA, toluene, rt, 82%; (vi) THF, 1-thioglycerol, Irgacure 2959, *hv*, 20 min, 70%; (vii) TC_{60}-alkyne, CuBr, PMDETA, toluene, rt, 80%; (viii) CF_3COOH, CH_2Cl_2, rt, 89%.

696, 575. $M_{n,NMR}$ = 4.1 kg/mol. SEC results: $M_{n,SEC}$ = 3.4 kg/mol, $M_{w,SEC}$ = 3.6 kg/mol, $Đ$ = 1.05.

DPOSS-CPS. To an open 20 mL vial were added VPOSS-CPS ($M_{n,NMR}$ = 4.1 kg/mol, $Đ$ = 1.05, 100 mg, 0.025 mmol, 1 equiv), 1-thioglycerol (27 mg, 0.25 mmol, 10 equiv), photoinitiator Irgacure 2959 (1 mg, 0.0045 mmol, 0.18 equiv), and 2 mL of THF. The mixture was then irradiated with UV (365 nm) for 20 min. The solution was then directly precipitated into methanol/water mixture (v/v = 1/1) twice, and the product was collected by filtration. After drying *in vacuo* the product was obtained as a white powder (83 mg). Yield: 70%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.34–6.42 (m, br, 140H), 5.32–4.40 (m, 16H), 4.21 (m, 2H), 3.92–3.47 (m, 21H), 3.46–2.92 (m, 8H), 2.91–2.42 (m, 36H), 2.41–1.32 (m, br, 86H), 1.27 (m, 2H), 1.22–0.77 (m, 20H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 173.3, 145.6, 130.2–126.1, 69.2, 68.0, 61.2, 50.2, 47.6–38.9, 33.7, 32.0, 30.3, 29.6, 28.7, 27.4, 22.6, 20.9. FT-IR (KBr) ν (cm^{-1}): 3345 (br), 3083, 3056, 3021, 2924, 2845, 1733, 1654, 1601, 1498, 1444, 1120 (Si–O–Si asymmetric stretching), 1024, 893, 770, 691, 542. $M_{n,NMR}$ = 4.9 kg/mol. SEC results: $M_{n,SEC}$ = 4.0 kg/mol, $M_{w,SEC}$ = 4.2 kg/mol, $Đ$ = 1.06.

TC_{60}-CPS. The CPS-N_3 ($M_{n,NMR}$ = 3.4 kg/mol, $Đ$ = 1.06, 100 mg, 0.03 mmol, 1 equiv), CuBr (1 mg, 0.007 mmol, 0.23 equiv), TC_{60}-alkyne (70 mg, 0.027 mmol, 0.9 equiv), and freshly distilled toluene (10 mL) were added into a 100 mL Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze–pump–thaw cycles, followed by introducing PMDETA (5 mg, 0.03 mmol, 1 equiv) under nitrogen protection. After one further freeze–pump–thaw cycle, the reaction was carried out for 16 h at room temperature. Then the crude mixture was directly applied onto a short column filled with a silica gel. Toluene/EA (v/v = 10/1) was first used as eluent to remove excessive CPS-N_3, and then the mixing solvent of CH_2Cl_2/EA (v/v = 2/1) was used to give resulting fraction. After removal of solvent, the mixture was precipitated in the methanol, collected by vacuum filtration, and dried *in vacuo* to afford the product as a red powder (131 mg). Yield: 80%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.26–6.44 (m, br, 140H), 5.02 (m, 2H), 4.87–4.53 (m, 20H), 4.48 (m, 2H), 3.99–3.83 (m, 5H), 3.39 (m, 4H), 2.96–2.46 (m, 10H), 2.45–1.25 (m, br, 178H), 0.94 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 165.6, 162.6, 145.8, 140.6, 129.2–125.1, 83.5, 63.2, 50.7, 46.8–39.6, 31.5, 29.6, 29.0, 28.1. FT-IR (KBr) ν (cm^{-1}): 3083, 3058, 3024, 2922, 2846, 1939, 1744, 1600, 1490, 1448, 1363, 1312, 1210, 1151, 1024, 837, 753, 702, 541. $M_{n,NMR}$ = 6.0 kg/mol. SEC results: $M_{n,SEC}$ = 4.5 kg/mol, $M_{w,SEC}$ = 4.7 kg/mol, $Đ$ = 1.05.

AC_{60}-CPS. TC_{60}-CPS ($M_{n,NMR}$ = 6.0 kg/mol, $Đ$ = 1.05, 100 mg, 0.017 mmol) was dissolved in mixture of 4 mL of CH_2Cl_2 and 1 mL of CF_3COOH. The resulting mixture was stirred at room temperature for 8 h. After removal of solvent, the residue was redissolved in 3 mL of benzene. After freeze-drying, the product was obtained as a red powder (80 mg). Yield: 89%. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 7.26–6.44 (m, br, 140H), 5.02 (m, 2H), 4.98–4.60 (m, 20H), 4.46 (m, 2H), 3.99–3.83 (m, 5H), 3.39 (m, 4H), 2.96–2.46 (m, 10H), 2.45–1.25 (m, br, 88H), 0.94 (m, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 165.6, 162.6, 145.8, 140.6, 129.2–125.1, 83.5, 62.7, 50.7, 46.8–39.6, 31.5, 29.6, 29.0. FT-IR (KBr) ν (cm^{-1}): 3082, 3060, 3026, 2925, 1958, 1745, 1645, 1601, 1493, 1453, 1431, 1364, 1203, 1122, 1066, 1028, 906, 759, 719, 540. $M_{n,NMR}$ = 5.4 kg/mol. SEC results: $M_{n,SEC}$ = 3.9 kg/mol, $M_{w,SEC}$ = 4.2 kg/mol, $Đ$ = 1.09.

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RESULTS AND DISCUSSION

Synthesis of the Linear PS Precursor. The synthetic route outlined in Scheme 1 is quite straightforward, aiming to fulfill the criteria of the "click" reaction, which requires only stoichiometric conditions, minimum setup and work-up procedures but achieves quantitative conversions.[17,23] The CuAAC reaction has been regarded as one of most widely used "click" reactions.[18,61] Since the first report to use the CuAAC reaction in the synthesis of a cyclic PS by Grayson et al.,[44] the CuAAC chemistry becomes prevalent in preparation of cyclic homopolymer,[46−49,62] cyclic block polymer,[56−58] and other cyclic polymer-based functionalized materials with complex architectures.[51,63−69] The synthesis of "diamond-ring-like" giant surfactants by tethering cyclic polymer with MNPs requires a functional CPS building block. To this end, an initiator (compound **2**) containing vinyl, alkyne, and bromo groups was specifically designed and synthesized, as illustrated in Scheme S2 of the Supporting Information. The chemical structure of **2** was unambiguously characterized by ^{1}H NMR and ^{13}C NMR (Figure S1). In the ^{1}H NMR spectrum, the resonance signals of vinyl and alkyne protons could be clearly observed at 5.89, 5.27, and 1.95 ppm, which could also be confirmed by the appearance of sp^2 and sp carbon at 134.1 and 117.4 ppm as well as 82.2 and 69.1 ppm in the ^{13}C NMR spectrum (Figure S1b).

Using this initiator, LPS-Br was readily prepared under the typical conditions for ATRP. After treating LPS-Br with sodium azide, a "clickable" azide group was installed at the chain end to give LPS-N_3. As shown in Figure 1a, the SEC curve reveals a monomodal and symmetric elution profile with narrow dispersity of LPS-N_3 ($Đ$ = 1.05). In the FT-IR spectrum, the absorbance band around 3300 and 2100 cm^{-1} verifies the successful introduction of alkyne and azide groups in the LPS-N_3 chain (Figure S2). Efforts to calculate the chain-end functionalities of LPS-N_3 or LPS-Br based on the ^{1}H NMR spectra were hampered by the fact that the resonance signals of the concerned protons cannot be fully deconvoluted from the other signals. Instead, the chain-end functionalities of LPS-N_3 were estimated from its MALDI-TOF mass spectrum. As shown in Figure S3a, only the mass distributions related to the structure of LPS-N_3 can be observed. Since the detection limit of MALDI-TOF is around 5%,[70] chain-end functionalities of LPS-N_3 are thus believed to be no less than 95%.

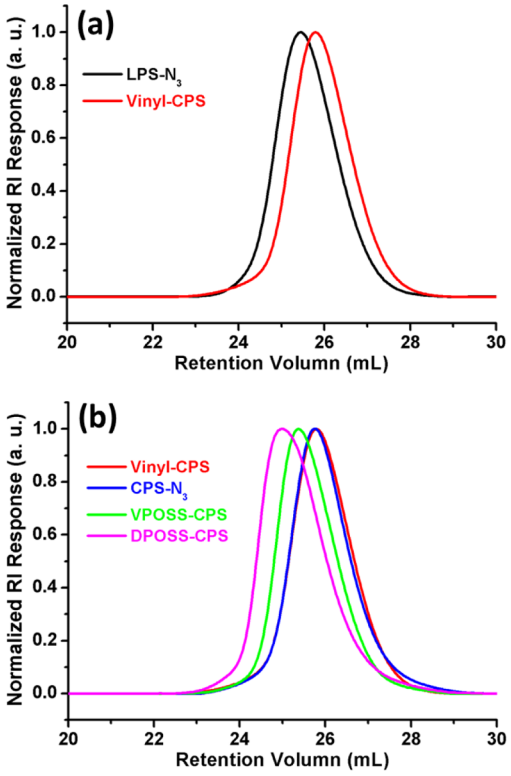

Figure 1. SEC overlay of (a) LPS-N_3 (black curve) and vinyl-CPS (red curve) and (b) Vinyl-CPS (red curve), CPS-N_3 (blue curve), VPOSS-CPS (green curve), and DPOSS-CPS (pink curve).

Synthesis of Vinyl-CPS via the CuAAC Chemistry. In the cyclization step, concentration of the starting linear polymer solution is the primary factor in determining the preference between intermolecular or intramolecular reactions.[44] The "click" cyclization reaction was carried out at a very dilute solution (0.3 mg/mL) to ensure fully intramolecular cyclization. Moreover, a continuous dropwise addition was utilized to maintain the infinitesimal concentration of linear polymer precursors during intramolecular cyclization.[44,71] Over a time period of 48 h, 300 mg of LPS-N_3 in a 20 mL toluene solution was slowly added into 1 L of warm toluene containing CuBr and PMDETA via syringe. After stirring for an additional 24 h, the reaction was completed, and the CPS product (Vinyl-CPS) was conveniently obtained by purification with flash column chromatography on silica gel.

The formation of Vinyl-CPS is unambiguously characterized by ^{1}H NMR, FT-IR, and SEC as well as MALDI-TOF mass spectrometry. The complete disappearance of azide and alkyne resonances in FT-IR spectra (Figure S2) provides the evidence of a successful CuAAC reaction. An increased retention volume of Vinyl-CPS relative to LPS-N_3 can be clearly seen in the SEC overlay (Figure 1a), which is corresponding with a smaller hydrodynamic volume of cyclic polymer, in comparison to their linear analogues.[42,44] The monomodal SEC profile with narrow distribution ($Đ$ = 1.07) remains, suggesting high uniformity of Vinyl-CPS with no byproducts of intermolecular reactions. The cyclization of LPS-N_3 to afford Vinyl-CPS was further confirmed by the MALDI-TOF mass spectroscopy. As shown in Figure S3a, two distinct molecular weight distributions corresponding to $[M + Ag]^+$ and $[M - N_2 + Ag]^+$ were observed for LPS-N_3, where $[M - N_2 + Ag]^+$ is caused by postsource expulsion of N_2 gas from the ionized LPS-N_3 sample.[72] After cyclization, the mass spectrum of Vinyl-CPS exhibits only one single symmetric distribution of $[M + Ag]^+$, where the molecule weight of Vinyl-CPS remains identical to its linear precursor polymer (see Figure S3). A representative peak m/z value of 2928.8 Da corresponding to 24-mer of CPS with a silver ion is in good agreement with the calculated mass ($[24\text{-mer}\cdot Ag]^+$, calcd mass 2928.4 Da) (Figure 2a). The difference between two neighboring peaks is equivalent to the mass of one styrene repeating unit (104.1 Da). These data clearly validate the precisely defined structure and molecular homogeneity of Vinyl-CPS. The yield of cyclization is as high as 80%, and the purification can be readily achieved by flash column chromatography with no fractionation required.

We have also applied dynamic light scattering (DLS) technique and diffusion-ordered spectroscopy (DOSY) to further confirm the success of cyclization. Although it is known that the R_h values of linear and cyclic polymers with the same molecular weights are different due to the lack of chain ends and thus a more compact chain conformation in cyclic

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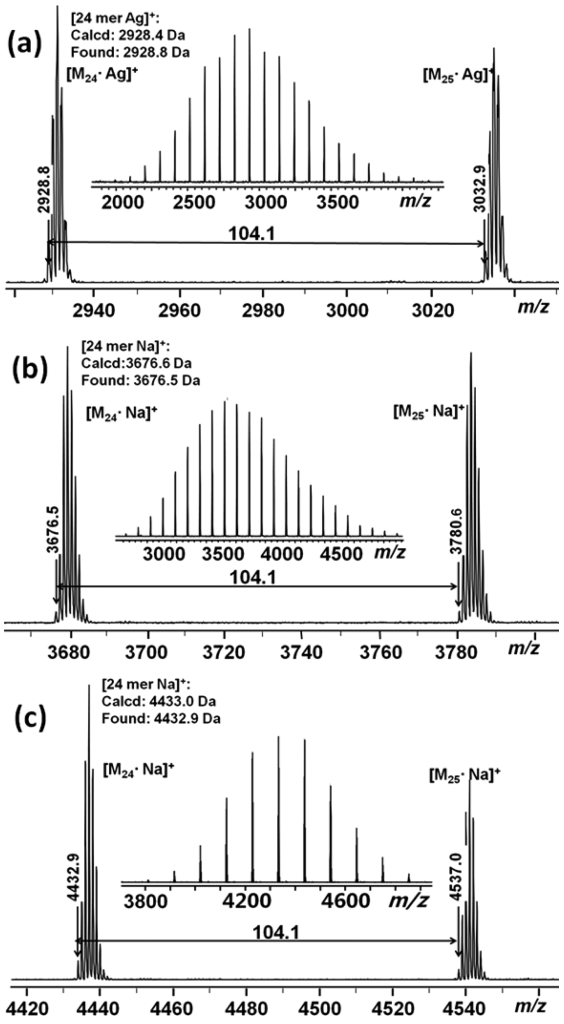

Figure 2. MALDI-TOF mass spectra of (a) Vinyl-CPS, (b) VPOSS-CPS, and (c) DPOSS-CPS. All these data were acquired with monoisotopic resolution. The insets show the full spectra.

polymers,[73] dynamic light scattering (DLS) results of the LPS-N_3 precursor and the Vinyl-CPS fail to give a clear difference in their R_h values (data not shown). This could be attributed to the low molecular weights of the polymers used in the demonstrative synthesis (~3000 Da), resulting in very small R_h difference in solution.[73] On the other hand, DOSY experiments of the LPS-N_3 and Vinyl-CPS indeed show that under the same conditions the diffusion constant (D) of the Vinyl-CPS is larger than that of the LPS-N_3 precursor (see Figure S4), which is qualitatively in good agreement with previously reported results.[74,75]

Synthesis of DPOSS-CPS via Thiol−Ene Chemistry. Thiol−ene addition reaction is another widely applied chemistry possessing mostly "click" features for various purposes.[19−21] It is particularly powerful for situations involving multiple functionalization or sites of poor reactivity such as polymer or dendrimers. The vinyl group[76] installed on Vinyl-CPS is subjected to the thiol−ene reaction to introduce an azide group in one step with high efficiency, affording the azido-functionalized cyclic PS building block. Efficient addition reaction between Vinyl-CPS and 2-azidoethanethiol was supported by the complete disappearance of the vinyl proton resonance peaks at 5.83 and 5.19 ppm and the appearance of resonances from the thiol−ether methylene protons at 3.44 and 2.70 ppm (Figure 3b). In addition, a strong absorption band appeared around 2100 cm^{-1} in the FT-IR spectra of the

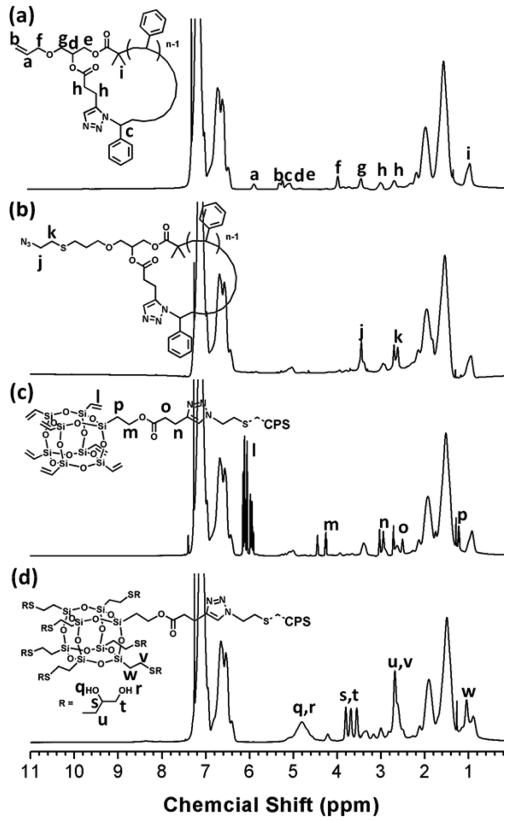

Figure 3. ^{1}H NMR spectra of (a) Vinyl-CPS, (b) CPS-N_3, (c) VPOSS-CPS, and (d) DPOSS-CPS.

resulting product (Figure S2), indicating the existence of the azide group. It should be noted that, via the thiol−ene reaction, the Vinyl-CPS precursor can be converted to other functional cyclic polymers with not only an azide group but also various other functional groups, such as hydroxyls and carboxylic acids,[24,26] enabling the as-prepared Vinyl-CPS as a common precursor. With azide-functionalized CPS (CPS-N_3) available, the general and efficient sequential "click" approach[26] would be applied to afford the desired "nano-diamond-ring-like" giant surfactants.

The CuAAC reaction between CPS-N_3 and VPOSS-alkyne proceeds at room temperature for overnight to achieve quantitative conjugation between the two building blocks. After purification by flash column chromatography on silica gel, the pure VPOSS-CPS was collected in a high yield (82%). In the ^{1}H NMR and ^{13}C NMR spectra of VPOSS-CPS, the signals of major characteristic protons and carbons attributing to vinyl groups of VPOSS can be clearly observed in Figure 3c (see also in Figure S5). In the FT-IR spectra (Figure S2), the disappearance of the azide absorption peak, as well as the appearance of a strong band at ca. 1123 cm^{-1} corresponding to the asymmetric stretching of Si−O−Si, is evident of successful reaction between CPS-N_3 and VPOSS-alkyne. The formation of VPOSS-CPS is also clearly exhibited in the SEC overlay (Figure 1b), where the curve of VPOSS-CPS shifts to lower retention volume comparing to CPS-N_3 due to increased molecular weight (Figure 1b). We also obtained the MALDI-TOF mass spectrum of VPOSS-CPS, as shown in Figure 2b, which

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Table 1. Summary of Molecular Characterizations

sample	molecular formula	M_{calcd} (Da)	M_{found} (Da)	$M_{n,NMR}$[c] (kg/mol)	$M_{n,SEC}$[d] (kg/mol)	$M_{w,SEC}$[d] (kg/mol)	$Đ$[d]
LPS-Br				3.3	3.3	3.4	1.04
LPS-N_3				3.3	3.3	3.4	1.05
Vinyl-CPS	$C_{207}H_{213}N_3AgO_5$[a]	2928.4[a]	2928.8[a]	3.3	3.1	3.3	1.07
CPS-N_3				3.4	3.1	3.3	1.06
VPOSS-CPS	$C_{230}H_{248}N_6NaO_{19}SSi_8$[b]	3676.6[b]	3676.5[b]	4.1	3.4	3.6	1.05
DPOSS-CPS	$C_{251}H_{304}N_6NaO_{33}S_8Si_8$[b]	4433.0[b]	4432.9[b]	4.9	4.0	4.2	1.06
TC_{60}-CPS				6.0	4.5	4.7	1.05
AC_{60}-CPS				5.4	3.9	4.2	1.09

[a]These data are based on 24-mer with a silver ion ([24-mer·Ag]$^+$). [b]These data are based on 24-mer with a sodium ion ([24-mer·Na]$^+$). [c]These data are calculated based on ^{1}H NMR spectra. [d]These data are obtained from SEC measurements.

displays only one symmetric molecular weight (MW) distribution. The isotopic MW observed from the mass spectrum agrees well with the calculated one. For example, the calculated isotopic MW for [24-mer·Na]$^+$ is 3676.6 Da, while the measured value is 3676.5 Da. The molecular characterization data are summarized in Table 1.

We have demonstrated that all the vinyl groups on the POSS cage could be efficiently and completely converted to various functional groups via the thiol−ene reaction.[24,26] Here, thiol−ene reactions were performed to install 14 hydroxyl groups onto the VPOSS cage to impart the hydrophilicity of giant surfactants, under the similar reaction conditions as reported in our previous publications.[26] The well-defined structure of the final giant surfactant DPOSS-CPS was unambiguously determined by NMR, SEC, and MALDI-TOF mass spectra. In the ^{1}H NMR spectra, complete disappearance of vinyl resonance peaks at 6.16−5.89 ppm and the emergence of new characteristic thiol ether protons resonance at 4.79, 3.80, 3.68, and 2.68 ppm reveal the complete addition reactions. Because of the larger hydrodynamic volume of DPOSS, in comparison to VPOSS, the SEC curve of DPOSS-CPS shifts to a lower retention volume than that of VPOSS-CPS, where the symmetric and monomodal peak with narrow dispersity was maintained. Strikingly, we even successfully obtained a clean MALDI-TOF mass spectrum of the final product DPOSS-CPS. One symmetric MW distribution was clearly exhibited in Figure 2c, where the observed MW is consistent with calculated one (e.g., for [24-mer·Na]$^+$, the found MW is 4432.9 Da, while the calculated MW is 4433.0 Da).

Extending to AC_{60}-CPS System. A perfect "ring" is designed to enable one to decorate it with various "diamonds" on the basis of specific designs. Similarly, the as-prepared cyclic PS ring is expected to be able to install not only functionalized POSS moieties but also other different "nanoatoms" ("diamonds") to construct a variety of giant surfactants. Benefiting from the modular synthetic design, CPS-N_3 is indeed a versatile building block that can be decorated with various alkyne-functionalized building blocks. Here, a precisely functionalized C_{60} derivative with one terminal alkyne and ten protected carboxylic acid groups (TC_{60}-alkyne)[27] was utilized as example to extend the versatility of CPS ring.

Because of the high polarity of TC_{60}-alkyne, a slightly excess amount of CPS-N_3 was used to ensure complete consumption of TC_{60}-alkyne. After the CuAAC ligation, the excess CPS-N_3 was readily removed by flash chromatography on silica gel using a mixture of toluene/EA (v/v = 10/1) as the eluent. The target product TC_{60}-CPS was eluted with CH_2Cl_2/EA (v/v = 2/1) and collected as a red powder after precipitation in methanol, filtering, and drying *in vacuo*. The disappearance of the absorption bands from azide group at ca. 2100 cm^{-1} and alkyne group at ca. 3300 cm^{-1} in the FT-IR spectra indicates successful reaction between CPS-N_3 and TC_{60}-alkyne (Figure S6). The well-defined structure of TC_{60}-CPS was further evidenced by ^{1}H NMR, ^{13}C NMR, and SEC (Figure 5). The amphiphilic features of final product, namely, AC_{60}-CPS, were endowed after deprotection of *tert*-butyl groups on TC_{60}, which was feasibly achieved by treating with CF_3COOH in CH_2Cl_2 without any further purification. The final products were fully characterized. The disappearance of *tert*-butyl protons at 1.47 ppm (Figure 4) in the ^{1}H NMR spectrum and *tert*-butyl

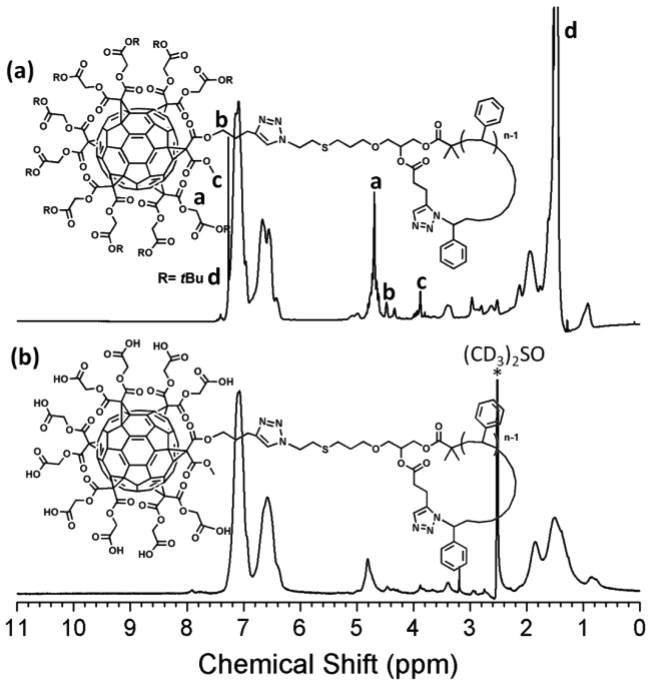

Figure 4. ^{1}H NMR spectra of (a) TC_{60}-CPS and (b) AC_{60}-CPS.

carbons at 28.2 and 82.9 ppm (Figure S7) confirms the complete deprotection. The well-defined structure of AC_{60}-CPS is also verified by the SEC overlay (Figure 5), where the curve of AC_{60}-CPS clearly shifts to higher retention volume after deprotection of *tert*-butyl groups, maintaining symmetric and monomodal peak with narrow dispersity. Notably, although the AC_{60}-CPS sample has ten carboxylic acid groups after deprotection, its SEC curve remains quite symmetric. This indicates that AC_{60}-CPS does not have significant interactions with the columns used in SEC experiments and is in agreement with our previous SEC results of either the APOSS-PS

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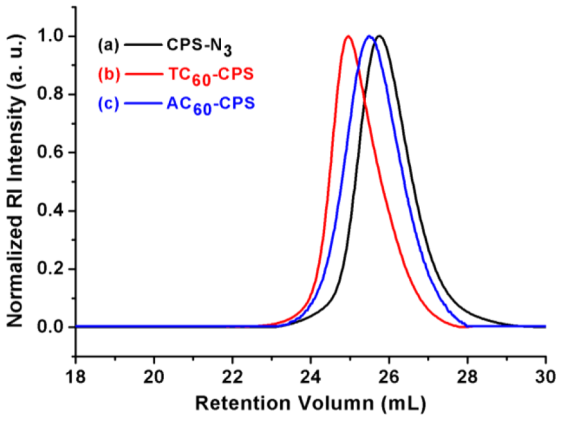

Figure 5. SEC overlay of (a) CPS-N_3 (black curve), (b) TC_{60}-CPS (red curve), and (c) AC_{60}-CPS (blue curve).

conjugates, where each APOSS cage has seven carboxylic acid groups,[26] or the AC_{60}-PS conjugates.[27] The data for molecular characterizations are summarized in Table 1.

It is anticipated that the functional CPS-N_3 building block should be applicable to "click" with various other "nanoatoms" bearing single or multiple alkyne groups, giving rise to giant surfactants with diverse and unique architectures. In fact, this CPS-N_3 has been employed in our group for preparation of nanoatom-based multiheaded/multitailed giant surfactants. The cyclic polymer based giant surfactants are expected to exhibit distinct self-assembling behaviors and create unique hierarchical structures in comparison to their linear analogues. For example, the giant surfactants composed of DPOSS tethered with a linear PS have been proved to be able to form ordered nanostructures with feature size around or smaller than 10 nm in bulk and thin films.[14] It is anticipated that owing to more compact polymer structure of CPS, DPOSS-CPS with the same PS molecular weight should construct nanostructures with even smaller periodicities than those of the DPOSS-LPS conjugates. Those sub-10 nm structures are not only of scientific interests but also of practical importance, since traditional top-down lithography techniques encounter serious challenges in achieving such small ordered domains.[77] The AC_{60}-based giant surfactants and their self-assembled micelles in solution might show potential applications in biology such as DNA cleavage[78] and enzyme inhibition[79] due to the interaction of water-soluble organofullerenes with DNA, proteins, and living cells.[80] The systematic investigation on the self-assembly behaviors of the nano-diamond-ring-like giant surfactants will be discussed in future publications.

CONCLUSION

In summary, two series of novel "nano-diamond-ring-like" giant surfactants based on hydrophilic DPOSS and AC_{60} tethered with a CPS tail have been successfully synthesized using a combination of the CuAAC and the thiol−ene "click" reactions. Vinyl-CPS was first prepared from a trifunctional linear PS precursor via the CuAAC "click" cyclization. Thiol−ene reaction was then applied to introduce an azide group onto the CPS, affording the cyclic CPS-N_3 building block to further react with alkyne-bearing building blocks, such as the VPOSS-alkyne and TC_{60}-alkyne. Because of the modular nature of the synthetic approach, it is expected that CPS-N_3 is compatible with any other alkyne-functionalized building blocks to construct a variety of nanomaterials. The resulting giant surfactants with cyclic polymer tails possess unique structural features other than their linear analogues. Study on their self-assembly behaviors is ongoing in our laboratory and will be discussed in future publications.

ASSOCIATED CONTENT

Supporting Information

Additional characterization data such as ^{13}C NMR spectra and FT-IR spectra of polymer products summarized in Table 1; experimental details and characterization of trifunctional initiator. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312−1319.
(2) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418−2421.
(3) Whitesides, G. M.; Boncheva, M. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 4769−4774.
(4) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell, T. P.; Rotello, V. M. *Nature* **2000**, *404*, 746−748.
(5) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−907.
(6) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **1996**, *35*, 1155−1196.
(7) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728−1731.
(8) Cui, H.; Chen, Z.; Zhong, S.; Wooley, K. L.; Pochan, D. J. *Science* **2007**, *317*, 647−650.
(9) Gröschel, A. H.; Schacher, F. H.; Schmalz, H.; Borisov, O. V.; Zhulina, E. B.; Walther, A.; Müller, A. H. E. *Nat. Commun.* **2012**, *3*, 710.
(10) Glotzer, S. C.; Solomon, M. J. *Nat. Mater.* **2007**, *6*, 557−562.
(11) Chen, Q.; Bae, S. C.; Granick, S. *Nature* **2011**, *469*, 381−384.
(12) Park, S.; Lim, J. H.; Chung, S. W.; Mirkin, C. A. *Science* **2004**, *303*, 348−351.
(13) Zhang, W.-B.; Yu, X.; Wang, C.-L.; Sun, H.-J.; Hsieh, I. F.; Li, Y.; Dong, X.-H.; Yue, K.; Van Horn, R.; Cheng, S. Z. D. *Macromolecules* **2014**, *47*, 1221−1239.
(14) Yu, X.; Yue, K.; Hsieh, I.-F.; Li, Y.; Dong, X.-H.; Liu, C.; Xin, Y.; Wang, H.-F.; Shi, A.-C.; Newkome, G. R.; Ho, R.-M.; Chen, E.-Q.; Zhang, W.-B.; Cheng, S. Z. D. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 10078−10083.
(15) Yu, X.; Zhong, S.; Li, X.; Tu, Y.; Yang, S.; Van Horn, R.; Ni, C. Y.; Pochan, D. J.; Quirk, R. P.; Wesdemiotis, C.; Zhang, W.-B.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2010**, *132*, 16741−16744.

(16) Wang, Z.; Li, Y.; Dong, X.-H.; Yu, X.; Guo, K.; Su, H.; Yue, K.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W.-B. *Chem. Sci.* **2013**, *4*, 1345−1352.
(17) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.
(18) Iha, R. K.; Wooley, K. L.; Nystrom, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620−5686.
(19) Hoyle, C. E.; Bowman, C. N. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540−1573.
(20) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.* **2010**, *39*, 1355−1387.
(21) Xi, W.; Scott, T. F.; Kloxin, C. J.; Bowman, C. N. *Adv. Funct. Mater.* **2014**, DOI: 10.1002/adfm.201302847.
(22) Kade, M. J.; Burke, D. J.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 743−750.
(23) Barner-Kowollik, C.; Du Prez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; Van Camp, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 60−62.
(24) Zhang, W.-B.; Li, Y.; Li, X.; Dong, X.-H.; Yu, X.; Wang, C.-L.; Wesdemiotis, C.; Quirk, R. P.; Cheng, S. Z. D. *Macromolecules* **2011**, *44*, 2589−2596.
(25) He, J.; Yue, K.; Liu, Y.; Yu, X.; Ni, P.; Cavicchi, K. A.; Quirk, R. P.; Chen, E.-Q.; Cheng, S. Z. D.; Zhang, W.-B. *Polym. Chem.* **2012**, *3*, 2112−2120.
(26) Yue, K.; Liu, C.; Guo, K.; Yu, X.; Huang, M.; Li, Y.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W.-B. *Macromolecules* **2012**, *45*, 8126−8134.
(27) Yu, X.; Zhang, W.-B.; Yue, K.; Li, X.; Liu, H.; Xin, Y.; Wang, C.-L.; Wesdemiotis, C.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2012**, *134*, 7780−7787.
(28) Yue, K.; Liu, C.; Guo, K.; Wu, K.; Dong, X.-H.; Liu, H.; Huang, M.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W.-B. *Polym. Chem.* **2013**, *4*, 1056−1067.
(29) Yue, K.; He, J.; Liu, C.; Huang, M.; Dong, X.-H.; Guo, K.; Ni, P.; Wesdemiotis, C.; Quirk, R.; Cheng, S. D.; Zhang, W.-B. *Chin. J. Polym. Sci.* **2013**, *31*, 71−82.
(30) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409−1430.
(31) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110*, 2081−2173.
(32) Laine, R. M. *J. Mater. Chem.* **2005**, *15*, 3725−3744.
(33) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431−1442.
(34) Kroto, H. W.; Heath, J. R.; Obrien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163.
(35) Zhang, W.-B.; Tu, Y.; Ranjan, R.; Van Horn, R.; Leng, S.; Wang, J.; Polce, M. J.; Wesdemiotis, C.; Quirk, R. P.; Newkome, G. R.; Cheng, S. Z. D. *Macromolecules* **2008**, *41*, 515−517.
(36) Hirsch, A. Frontmatter. In *The Chemistry of the Fullerenes*; Wiley-VCH Verlag GmbH: Weinheim, 2008; pp I−XI.
(37) Hirsch, A.; Vostrowsky, O. *Eur. J. Org. Chem.* **2001**, 829−848.
(38) J. Feher, F.; D. Wyndham, K.; K. Baldwin, R.; Soulivong, D.; W. Ziller, J.; D. Lichtenhan, J.; D. Lichtenhan, J. *Chem. Commun.* **1999**, 1289−1290.
(39) Li, Y.; Guo, K.; Su, H.; Li, X.; Feng, X.; Wang, Z.; Zhang, W.; Zhu, S.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W.-B. *Chem. Sci.* **2014**, *5*, 1046−1053.
(40) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041−2044.
(41) Jia, Z.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2085−2097.
(42) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009**, *38*, 2202−2213.
(43) Yamamoto, T.; Tezuka, Y. *Polym. Chem.* **2011**, *2*, 1930−1941.
(44) Laurent, B. A.; Grayson, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 4238−4239.
(45) Boydston, A. J.; Xia, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12775−12782.
(46) Binauld, S.; Hawker, C. J.; Fleury, E.; Drockenmuller, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 6654−6658.
(47) Hoskins, J. N.; Grayson, S. M. *Macromolecules* **2009**, *42*, 6406−6413.
(48) Qiu, X. P.; Tanaka, F.; Winnik, F. M. *Macromolecules* **2007**, *40*, 7069−7071.
(49) Shi, G.-Y.; Pan, C.-Y. *Macromol. Rapid Commun.* **2008**, *29*, 1672−1678.
(50) Zhang, K.; Lackey, M. A.; Cui, J.; Tew, G. N. *J. Am. Chem. Soc.* **2011**, *133*, 4140−4148.
(51) Lonsdale, D. E.; Monteiro, M. J. *Chem. Commun.* **2010**, *46*, 7945−7947.
(52) Zhu, X.; Zhou, N.; Zhang, Z.; Sun, B.; Yang, Y.; Zhu, J.; Zhu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 6615−6618.
(53) Zhu, X.; Zhou, N.; Zhu, J.; Zhang, Z.; Zhang, W.; Cheng, Z.; Tu, Y.; Zhu, X. *Macromol. Rapid Commun.* **2013**, *34*, 1014−1019.
(54) Glassner, M.; Blinco, J. P.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2011**, *32*, 724−728.
(55) Honda, S.; Yamamoto, T.; Tezuka, Y. *J. Am. Chem. Soc.* **2010**, *132*, 10251−10253.
(56) Eugene, D. M.; Grayson, S. M. *Macromolecules* **2008**, *41*, 5082−5084.
(57) Poelma, J. E.; Ono, K.; Miyajima, D.; Aida, T.; Satoh, K.; Hawker, C. J. *ACS Nano* **2012**, *6*, 10845−10854.
(58) Zhang, B.; Zhang, H.; Li, Y.; Hoskins, J. N.; Grayson, S. M. *ACS Macro Lett.* **2013**, *2*, 845−848.
(59) Wan, X.; Liu, T.; Liu, S. *Biomacromolecules* **2011**, *12*, 1146−1154.
(60) Zhang, W.-B.; Sun, F.; Tirrell, D. A.; Arnold, F. H. *J. Am. Chem. Soc.* **2013**, *135*, 13988−13997.
(61) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−+.
(62) Lu, D.; Jia, Z.; Monteiro, M. J. *Polym. Chem.* **2013**, *4*, 2080−2089.
(63) Hossain, M. D.; Valade, D.; Jia, Z. F.; Monteiro, M. J. *Polym. Chem.* **2012**, *3*, 2986−2995.
(64) Jia, Z.; Lonsdale, D. E.; Kulis, J.; Monteiro, M. J. *ACS Macro Lett.* **2012**, *1*, 780−783.
(65) Kulis, J.; Jia, Z.; Monteiro, M. J. *Macromolecules* **2012**, *45*, 5956−5966.
(66) Lonsdale, D. E.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4603−4612.
(67) Jiang, X.; Shi, Y.; Zhu, W.; Chen, Y.; Xi, F. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 4239−4245.
(68) Sugai, N.; Heguri, H.; Ohta, K.; Meng, Q. Y.; Yamamoto, T.; Tezuka, Y. *J. Am. Chem. Soc.* **2010**, *132*, 14790−14802.
(69) Ko, Y. S.; Yamamoto, T.; Tezuka, Y. *Macromol. Rapid Commun.* **2014**, *35*, 412−416.
(70) Lewis, J. K.; Wei, J.; Siuzdak, G. *Encyclopedia of Analytical Chemistry*; John Wiley & Sons: New York, 2000.
(71) Harth, E.; Van Horn, B.; Lee, V. Y.; Germack, D. S.; Gonzales, C. P.; Miller, R. D.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 8653−8660.
(72) Li, Y.; Hoskins, J. N.; Sreerama, S. G.; Grayson, S. M. *Macromolecules* **2010**, *43*, 6225−6228.
(73) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: Oxford, 2003.
(74) Griffiths, P. C.; Stilbs, P.; Yu, G. E.; Booth, C. *J. Phys. Chem.* **1995**, *99*, 16752−16756.
(75) Edwards, C. J. C.; Stepto, R. F. T.; Semlyen, J. A. *Polymer* **1980**, *21*, 781−786.
(76) Northrop, B. H.; Coffey, R. N. *J. Am. Chem. Soc.* **2012**, *134*, 13804−13817.
(77) Lin, B. J. *J. Micro/Nanolith MEMS MOEMS* **2004**, *3*, 377−395.
(78) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918−7919.
(79) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506−6509.
(80) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807−815.