“CLICKING” FLUORIATED POLYHEDRAL OLIGOMERIC SILSEQUIOXANE
ONTOPOLYMERS: A MODULAR APPROACH TOWARD SHAPE AMPHIPHILES
WITH FLUOROUS MOLECULAR CLUSTERS

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“CLICKING” FLUORIATED POLYHEDRAL OLIGOMERIC SILSEQUIOXANE ONTO POLYMERS: A MODULAR APPROACH TOWARD SHAPE AMPHIPHILES WITH FLUOROUS MOLECULAR CLUSTERS

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Thesis

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ABSTRACT

Convenient synthesis of fluorinated molecular nanoparticles constitutes a major challenge in the preparation of fluoro shape amphiphiles. To facilitate a modular and efficient synthesis, a “clickable” fluorinated polyhedral oligomeric silsesquioxane equipped with seven $1H,1H,2H,2H$-heptadecafluorodecyl side chains and one alkyne group on its periphery (FPOSS-alkyne) was designed and synthesized. It was then used to prepare a series of FPOSS-containing polymers with various architectures via “click” chemistry. FPOSS was tethered onto either homo-polystyrene (PS) or polystyrene-block-poly(ethylene oxide) (PS-b-PEO) at precise locations, including chain end (FPOSS-PS, FPOSS-PS-b-PEO), junction point [PS-(FPOSS)-PEO], or distributed along a PS chain (PS/FPOSS). This study demonstrates the chemical robustness of the novel building block and establishes a general and efficient approach to introduce fluororous molecular clusters onto polymers, especially high molecular weight polymers or those with high fluoro contents. These precisely defined FPOSS-containing polymers could serve as model compounds to study the self-assembly behaviors of these shape amphiphiles in the bulk, solution and thin film states.
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Fluorous materials have received remarkable attention in a broad range of practical applications including self-cleaning and anti-fouling coatings, non-wetting fabrics, smart surfaces and others, due to their low surface energy, high density, notable thermal stability, and excellent chemical inertness.\textsuperscript{1-5} The most unique property of fluorous materials is omniphobicity, which refers to simultaneous hydrophobicity and oleophobicity, originated from their ultra-low surface energy.\textsuperscript{6} The fluorous phase has thus been considered as the “third” phase, that repels both oil and water.\textsuperscript{7} Incorporation of fluorinated component into macromolecules is anticipated to bring novel self-assembly behaviors in the bulk, solution and thin film states, which are not only academically intriguing but also technological relevant.\textsuperscript{8-13} Among them, fluorous molecular clusters are of particular interest.

Fluorinated [60]fullerene (C\textsubscript{60}) or polyhedral oligomeric silsesquioxane (POSS) are two families of fluorous molecular clusters and have attracted much interests, due mainly to their precisely defined nanoscale shape and volume and high fluoro functionalities at the peripheries of the particles.\textsuperscript{14-19} Gakh \textit{et al.} reported the first attempt of fluorination of [60]fullerene (C\textsubscript{60}).\textsuperscript{14} The adduct, C\textsubscript{60}F\textsubscript{48} however, was found to be unstable in
solutions. Recently, Mabry’s group developed a series of fluorinated POSS nanoparticles possessing eight fluoroalkyl chains of varying chain lengths on the vertexes of POSS cage via direct condensation of perfluorinated siloxanes. Among them, octakis(1H,1H,2H,2H-heptadecafluorodecyl)-POSS was reported to be one of crystalline solids having the lowest surface energy, and was utilized to create superoleophobic surfaces by blending with polymers. Due to high immiscibility between fluorinated POSS units and polymer matrix, however, these blends usually suffer from macro-phase separation that reduces their surface robustness. The poor solubility in common solvents also limits their practical applications.

Covalently incorporating fluorinated POSS (FPOSS) into polymer chains has been proposed to increase their compatibility and processability. FPOSS compounds equipped with highly reactive functional groups are thus desired for further derivatization. Ramirez et al. recently reported the synthesis of functionalized FPOSS possessing alkyl, aryl, or acrylate moieties through a delicate incomplete condensation method. The acrylate functionalized fluorinated POSS was then used as a macro-monomer to copolymerize with methyl methacrylate (MMA) using reversible addition-fragmentation chain transfer (RAFT) technique. This approach, however, alters the original silicon-oxygen frame and breaks the symmetry of POSS core. Moreover, copolymerization usually has poor control upon the location and number of FPOSS within polymer chains due to varying reactivity originated from different steric hindrance of the local bulky volume.

Recently, we have developed a highly efficient and modular “thiol-ene” approach for syntheses of POSS based shape amphiphiles. As a precursor, a heptavinyl POSS
(VPOSS) was connected to polymer chains of diverse architectures via either a “grafting-to” or “grafting-from” approach.\textsuperscript{21,25} Further, the thiol-ene reaction between these VPOSS-containing precursors with thiol ligands quantitatively converts VPOSS into various functional POSS. For example, a facile synthesis of FPOSS-containing polymers has been reported using a combination of ring-opening polymerization (ROP), anionic polymerization, hydrosilylation, and “thiol-ene” reaction.\textsuperscript{21} This “post-functionalization” strategy enables the installation of different functionalities onto the same VPOSS-polymer precursors with high efficiency.\textsuperscript{27} However, when bulky ligands, such as the fluoroalkyl thiols, are installed, undesired coupling reactions between the polymers may occur during the thiol-ene reaction and produce dimers as evidenced in the SEC chromatographs.\textsuperscript{21,25} The dimer formation has been observed to increase when the molecular weight of polymers is high and/or when products of high fluoro-content are targeted.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{FPOSS-containing polymers with various architectur}
\end{figure}
In this work, we propose the use of a “clickable” fluorous cluster based on POSS (FPOSS-alkyne, see below) to address this problem and report the design and synthesis of FPOSS-containing polymers with diverse topologies using copper catalyzed Huisgen [3+2] cycloaddition (CuAAC) click chemistry.\textsuperscript{32,33} The method is modular, efficient, and robust. By carefully choosing polymer precursors with azide groups, a series of FPOSS-containing polymers was prepared where the FPOSS units are precisely located at chain-end, the junction point, or along a polymer chain of either homo-polystyrene (PS) or polystyrene-\textit{block}-poly(ethylene oxide) (PS-\textit{b}-PEO) (Scheme 1).
CHAPTER II

CHEMICALS AND SOLVENTS

Chemicals and Solvents. The following chemicals are used as received: sodium azide (NaN₃, Aldrich, ReagentPlus®, > 99.5%), N, N-dimethylformamide (DMF, Aldrich, 99.9%), methanol (MeOH, Fisher Scientific, reagent grade), 3,3,4,4,5,5,6,7,8,8,9,9,10,10,10-heptadecafluorodecane-1-thiol (F₈-SH, Aldrich, 98%), N,N’-diisopropylcarbodiimide (DIPC, Aldrich, 99%), α,α,α-trifluorotoluene (TFT, Aldrich, ≥ 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), deuterated chloroform (CDCl₃, Aldrich, 99.8 atom % D), N,N,N’,N’’,N’’’-pentamethyldiethylene-triamine (PMDETA, Aldrich, 99%). 2,2’-Azobisisobutyronitrile (AIBN, Aldrich, 98%) was purified by recrystallization from ethanol. Cuprous bromide (CuBr, Aldrich, 98%) was purified by stirring in acetic acid overnight, washed with acetone for three times, and dried in vacuum. Chloroform (CHCl₃, Fisher Scientific, reagent grade), styrene (Aldrich, 99%), and 4-vinyl benzyl chloride (VBC, Aldrich, > 90%) were purified by stirring over calcium hydride for 12 hours and redistilled under vacuum before use. VPOSS-OH and S-1-dodecyl-S’-(r,r’-dimethyl-r’’-acetic acid)trithiocarbonate (TC) was synthesized according to the references. The
carboxylic acid group on TC was further capped with ethanol to give an ester (ETC), as described in Electronic Supplementary Information (ESI). Preparation of the azide functionalized polymers, PS-N$_3$, PEO-$b$-PS-N$_3$, and PS-(N$_3$)-PEO, can be found in the literatures.$^{36,37}$ Synthesis of 4-oxo-4-(prop-2-yn-1-yl)oxy) butanoic acid is described in ESI.
CHAPTER III

INSTRUMENTATION AND CHARACTERIZATIONS

All $^1$H and $^{13}$C NMR spectra were acquired in CDCl$_3$ using a Varian 500 NMR spectrometer. The $^1$H NMR spectra were referenced to the residual proton impurities in the CDCl$_3$ at $\delta$ 7.27 ppm. The $^{13}$C NMR spectra were referenced to $^{13}$CDCl$_3$ at $\delta$ 77.00 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films onto KBr plates from polymer solutions. The data were processed using Win-IR software.

Size-exclusion chromatographic analyses (SEC) 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 double detector system with THF as eluent at a flow rate of 1.0 mL/min at 30 °C; the detector system consisted of a differential refractometer (Waters 410) and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda$= 670 nm). Regular SEC calibrations were conducted with polystyrene standards (Polymer Laboratories).

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics,
Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector.
4.1 FPOSS-OH

VPOSS-OH (200 mg, 0.33 mmol) and DMPA (5.0 mg) were dissolved in a mixture solvent of chloroform and TFT (1:3, v/v). F$_8$-SH (2.06 g, 4.62 mmol) was then added. The solution was irradiated under UV 365 nm for 30 min. The crude product was purified by silica gel column. FPOSS-OH was obtained by eluting with a mixture of chloroform and hexane (1:1, v/v) (0.80 g, 65%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, $\delta$): 3.82 (t, 2H, -SiCH$_2$C$_2$OH), 2.50-2.85 (m, 28H, -C$_2$H$_2$SC$_2$H$_2$-), 2.20-2.38 (m, 14H, -CH$_2$CF$_2$-), 1.17 (t, 2H, -SiCH$_2$CH$_2$OH), 1.06 (t, 14H, -SiCH$_2$CH$_2$S-). FT-IR (cm$^{-1}$): 2920, 1532, 1442, 1366, 1331, 1203, 1148, 1111, 1026, 954, 871, 797, 738, 705, 652, 559, 530, 471. MS (MALDI-TOF, Da): Calc: 4032.83, Found: 4033.04 (M$\cdot$Na)$^+$. 
4.2 FPOSS-alkyne

FPOSS-OH (0.80 g, 0.2 mmol), 4-oxo-4-(prop-2-yn-1-yloxy) butanoic acid (62.4 mg, 0.4 mmol), and DMAP (10 mg, 0.08 mmol) was dissolved in 30 mL of mixture of dichloromethane and TFT (1:3, v/v). DIPC (25 mg, 0.2 mmol) was then added dropwise under 0 °C. The solution was stirred at room temperature for 24 hours. After removal of solvent with rotatory evaporator, the crude product was purified by silica gel column. FPOSS-alkyne was obtained by eluting with a mixture eluent of chloroform and hexane (1:1, v/v) (0.60 g, 72%). \(^1\)H NMR (CDCl\(_3\), 500M, ppm, δ): 4.70 (d, 2H, -COOC\(_2\)H\(_2\)C\(_2\)H), 4.20 [t, 2H, -SiCH\(_2\)OC(O)-], 2.50-2.85 (m, 28H, -C\(_2\)H\(_2\)SC\(_2\)H\(_2\)-), 2.60 [t, 4H, -OC(O)CH\(_2\)CH\(_2\)COO-], 2.45 (t, 1H, -CH\(_2\)C\(_2\)H), 2.20-2.38 (m, 14H, -CH\(_2\)CF\(_2\)-), 1.17 (t, 2H, -SiCH\(_2\)CH\(_2\)O-), 1.06 (t, 14H, -SiCH\(_2\)CH\(_2\)S-). FT-IR (cm\(^{-1}\)): 2926, 1738 (C=O), 1648, 1441, 1365, 1331, 1203, 1149, 1113, 955, 868, 795, 737, 705, 652, 557, 530, 472. MS (MALDI-TOF, Da): Calc: 4170.87, Found: 4171.39 (M∙Na).^+ 

4.3 PS/Cl

MTC (40 mg, 0.10 mmol), styrene (4.0 g), VBC (0.3 g), AIBN (2 mg, 0.01 mmol), and 4 mL of anhydrous toluene were added into a reaction flask equipped with a magnetic stirrer. The flask was degassed by three freeze-vacuum-thaw cycles and immersed into a 110 °C oil bath. After a prescribed time, the flask was quenched by liquid nitrogen. By
adding the polymer solution into an excess of cold methanol, PS/Cl was precipitated and collected by filtration. The polymer was obtained after drying in vacuo for 24 h (1.8 g, 41.2%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, $\delta$): 6.30-7.40 (br, 1200H, aromatic H), 4.52 (br, 20H, -CH$_2$Cl), 3.30 (br, 2H, CH$_3$CH$_2$O-), 1.67-2.15 [br, 240H, -CH$_2$CH(-Ar)-], 1.20-1.67 [br, 480H, -CH$_2$CH(-Ar)-], 0.90-1.10 [m, 31H, -O(C=O)C(CH$_3$)$_2$CH$_2$-], -S(CH$_2$)$_{11}$CH$_3$]. FT-IR (cm$^{-1}$): 3082, 3059, 3026, 2922, 2875, 1945, 1872, 1790, 1601, 1490, 1453, 1371, 1264, 1176, 1069, 1030, 913, 767, 735, 697, 540. SEC (THF, RI detector): $M_n = 23,000$ g/mol, $M_w = 23,700$ g/mol, PDI = 1.03.

4.4 PS/N$_3$

PS/Cl (23,000 g/mol, $N_{Cl} = 10$, 1.5 g, 0.065 mmol), NaN$_3$ (81 mg, 1.25mmol), and anhydrous DMF (5 mL) were added into a round bottle flask with a magnetic stirrer. After stirred for 24 hours, the mixture was diluted with 100 mL of chloroform and washed with water for three times. The organic layer was collected and dried under anhydrous Na$_2$SO$_4$. After removal of excess solvent, the product was repeatedly precipitated into cold methanol. PS/N$_3$ was obtained after drying in vacuo for 24 h (1.2 g, 80%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, $\delta$): 6.30-7.40 (br, 1200H, aromatic H), 4.25 (br, 20H, -CH$_2$N$_3$), 3.30 (br, 2H, CH$_3$CH$_2$O-), 1.67-2.15 [br, 240H, -CH$_2$CH(-Ar)-], 1.20-1.67 [br, 480H, -CH$_2$CH(-Ar)-], 0.90-1.10 [m, 31H, -O(C=O)C(CH$_3$)$_2$CH$_2$-, -S(CH$_2$)$_{11}$CH$_3$]. FT-IR (cm$^{-1}$): 3082, 3060, 3026, 2883, 2098 (-N$_3$), 1945, 1872, 1800, 1724, 1601,
1493, 1450, 1453, 1369, 1068, 1026, 909, 757, 734, 698, 540. SEC (THF, RI detector): $M_n = 16.0 \text{ kg/mol, } M_w = 18.1 \text{ kg/mol, } \text{PDI} = 1.11.$

4.5 FPOSS-PS

PS-N$_3$ ($M_n = 2400 \text{ g/mol, } 55 \text{ mg, } 0.023 \text{ mmol}$), FPOSS-alkyne (80 mg, 0.02 mmol), CuBr (2 mg, 0.02 mmol), and 15 mL of TFT were added into an Schlenk flask. After three freeze–pump–thaw cycles, PMDETA (4 mg, 0.02 mmol) was introduced into the flask under nitrogen protection. After stirring overnight at room temperature, the excess PS-N$_3$ was removed with silica gel column by eluted with chloroform. Further eluted with a mixture of chloroform and methanol (98:2, v/v) gives the product. The solution was concentrated and precipitated in the cold methanol for three times. The product, FPOSS-PS, was collected as white powder (98 mg, 75%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, δ): 6.30-7.40 (br, 120H, phenyl rings), 5.15 [m, 3H, -CH$_2$CH(Ar)N-; triazole-CH$_2$O-], 4.20 [br, 2H, -(C=O)OCC$_2$H$_2$Si-], 3.40-3.75 [m, 2H, CH$_3$CH$_2$O(C=O)-], 2.50-2.85 (m, 28H, -CH$_2$SCH$_2$-), 2.50 [br, 4H, -OC(O)CH$_2$CH$_2$COO-], 2.20-2.38 (m, 14H, -CH$_2$CF$_2$-), 1.67-2.15 [br, 24H, -CH$_2$CH(-Ar)-], 1.20-1.67 [br, 48H, -CH$_2$CH(-Ar)-], 0.80-1.20 [m, 25H, -SiCH$_2$CH$_2$-; CH$_3$CH$_2$O(C=O)-; O(C=O)C(CH$_3$)$_2$CH$_2$-]. FT-IR (cm$^{-1}$): 3082, 3061, 3027, 2926, 2852, 1944, 1872, 1800, 1732 (C=O), 1601, 1493, 1450, 1364, 1238, 1205, 1147, 1028, 955, 871, 754, 699, 652, 532, 465. SEC (THF, RI detector): $M_n = 4800 \text{ g/mol, } M_w = 5400 \text{ g/mol, } \text{PDI} = 1.12.$ MS (MALDI-TOF, Da): Calc: 5868.71, Found: 5869.17 (M$_{14}$·Ag$^+$).
PS/N$_3$ ($M_n = 23,000$ g/mol, 100 mg, 0.004 mmol, $n_{azide} = 0.04$ mmol), FPOSS-alkyne (180 mg, 0.043 mmol), CuBr (5 mg, 0.035 mmol), and 10 mL of TFT were added into a Schlenk flask. After three freeze–pump–thaw cycles, PMDETA (12.0 mg, 0.07 mmol) was introduced into the flask under nitrogen protection. After stirring overnight at room temperature, the excess FPOSS-alkyne was removed with silica gel column by eluted with chloroform. Further eluted with a mixture of chloroform and methanol (95:5, v/v) gives the product. The solution was concentrated and precipitated in the cold methanol for three times (200 mg, 71.4%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, $\delta$): 6.30-7.40 (br, 1200H, aromatic H), 5.28 (br, 20H, -CH$_2$-triazole-), 5.15 (br, 20H, -triazole-CH$_2$O-), 4.15 [br, 20H, -(C=O)OCCH$_2$CH$_2$Si-], 2.50-2.85 (m, 280H, -CH$_2$SCH$_2$-), 2.50 [br, 40H, -OC(O)CH$_2$CH$_2$COO-], 2.20-2.38 (m, 140H, -CH$_2$CF$_2$-), 1.67-2.15 [br, 240H, -CH$_2$CH(-Ar)-], 1.20-1.67 [br, 480H, -CH$_2$CH(-Ar)-], 0.90-1.10 [m, 31H,-O(C=O)C(CH$_3$)$_2$CH$_2$-, -S(CH$_2$)$_1$CH$_3$]. FT-IR (cm$^{-1}$): 3082, 3061, 3026, 2925, 2853, 1944, 1884, 1807, 1736 (C=O), 1602, 1493, 1450, 1364, 1238, 1206, 1748, 1029, 956, 754, 699, 653, 558, 532.

SEC (THF, RI detector): $M_n = 79,000$ g/mol, $M_w = 89,000$ g/mol, PDI = 1.12.
4.7 FPOSS-PS-b-PEO

PEO-\textit{b}-PS-N$_3$ (100 mg, 0.02 mmol, $M_n^{\text{PS}} = 2800$ g/mol, $M_n^{\text{PEO}} = 2000$ g/mol), FPOSS-alkyne (102 mg, 0.024 mmol), CuBr (3 mg, 0.024 mmol), and 15 mL of TFT were added into a Schlenk flask. After three freeze–pump–thaw cycles, PMDETA (4 mg, 0.024 mmol) was introduced into the flask under nitrogen protection. After stirring overnight at room temperature, the excess FPOSS-alkyne was removed by eluting from silica gel column with chloroform. Further elution with a mixture of chloroform and methanol (95:5, v/v) gives the product. The solution was concentrated and the product was precipitated into cold hexanes for three times. After filtration, the product was collected as white powder (142 mg, 71% yield). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, $\delta$): 6.30-7.40 (br, 140 H, aromatic H), 5.15 [m, 3H, -CH(-Ar)N; triazole-CH$_2$O-], 4.20 [br, 2H, -(C=O)OCCH$_2$CH$_2$Si-], 3.50-3.80 (m, 180H, -CH$_2$CH$_2$O-), 3.40 (s, 3H, CH$_3$O-), 2.50-2.85 (m, 28H, -CH$_2$SCH$_2$-), 2.50 [br, 4H, -OC(O)CH$_2$CH$_2$COO-], 2.20-2.40 (m, 14H, -CH$_2$CF$_2$-), 1.70-2.20 [br, 28H, -CH$_2$CH(-Ar)-], 1.20-1.67 (br, 56H, -C$_2$H$_5$CH(-Ar)-), 0.80-1.20 [m, 25H, -SiCH$_2$CH$_2$-; CH$_3$CH$_2$O(C=O)-; O(C=O)C(CH$_3$)$_2$CH$_2$-]. FT-IR (cm$^{-1}$): 3082, 3060, 3026, 2920, 2872, 1944, 1884, 1807, 1733 (C=O), 1601, 1491, 1450, 1351, 1242, 1205, 1114, 1053, 1029, 953, 758, 700, 660, 531. SEC (THF, RI detector): $M_n = 11,000$ g/mol, $M_w = 12,300$ g/mol, PDI = 1.11.
4.8 PS-(FPOSS)-PEO

The “click” reaction was carried out in a similar procedure to that of FPOSS-PS-\(b\)-PEO in 75% yield from PS-(N\(_3\))-PEO (\(M_{n}^{PS} = 5200\) g/mol, \(M_{n}^{PEO} = 2000\) g/mol). \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm, \(\delta\)): 7.50 (1H, br, triazole), 6.30-7.40 (br, 260H, aromatic H), 5.20 (s, 2H, triazole-\(CH_2O\)-), 4.6-4.7 [1H, br, -\(CH\)(-Ar)Br], 4.18-4.4 [br, 3H, -(C=O)OCCH\(_2\)CH\(_2\)Si-; -OCH\(_2\)CH(CH\(_2\)N-)O-], 3.50-3.80 (m, 180H, -\(CH_2CH_2O\)-), 3.40 (s, 3H, CH\(_3\)O-), 3.00-3.20 (2H, br, -CH\(_2\)N-), 2.50-2.85 (m, 28H, -\(CH_2SCH_2\)-), 2.50 [br, 4H, -OC(O)CH\(_2\)CH\(_2\)COO-], 2.20-2.40 (m, 14H, -\(CH_2CF_2\)-), 1.70-2.20 [br, 52H, -\(CH_2CH\)(-Ar)-], 1.20-1.67 (br, 104H, -\(CH_2CH\)(-Ar)-], 0.80-1.20 [m, 25H, -Si\(CH_2CH_2\)-; \(CH_3CH_2O(C=O)-;\) O(C=O)C(CH\(_3\)_2CH\(_2\)-]. FT-IR (cm\(^{-1}\)): 3082, 3060, 3026, 2923, 2871, 1945, 1884, 1807, 1734 (C=O), 1601, 1491, 1450, 1352, 1284, 1242, 1206, 1146, 1115, 1029, 953, 758, 700, 652, 536, 463. SEC (THF, RI detector): \(M_n = 14,000\) g/mol, \(M_w = 15,200\) g/mol, PDI = 1.08.
5.1 FPOSS-alkyne as a “Clickable” Fluorous Molecular Cluster.

In order to take advantage of highly efficient CuAAC “click” reaction, FPOSS with an azide or alkyne functionality is desired. Considering that polymers with azide group can be readily prepared by a combination of controlled/living radical polymerization and nucleophilic substitution with sodium azide, an alkyne-functionalized FPOSS with long fluoroalkyl side chains could be a model building block to construct FPOSS-containing polymers with various architectures (Scheme 1). “Thiol-ene” reaction provides an efficient approach to install different functional groups onto VPOSS-OH precursors. Long fluoroalkyl thiol ligands, however, usually suffer from their poor solubility in common solvents and thus, a complete installation of fluoroalkyl chains on VPOSS is difficult since the resulting partially fluorinated POSS units tend to precipitate out of the solution during the reaction. A fluorous solvent, α,α,α-trifluorotoluene (TFT), was then used to enhance their solubility. The synthetic route of FPOSS-alkyne is illustrated in
Scheme 2. VPOSS-OH was first coupled with fluoroalkyl thiol ligands, F₈-SH, to generate FPOSS bearing seven heptadecafluorodecyl side chains and one hydroxyl group (FPOSS-OH). Further esterification with 4-oxo-4-(prop-2-yn-1-yloxy) butanoic acid afforded FPOSS-alkyne with reasonable yield (72%). A long linkage between alkyne and FPOSS cage was designed to increase the reactivity of terminal functional group, since the alkyne group may be buried inside of the bulky fluoroalkyl chains and have limited accessibility.

Reagents and Conditions: (i) F₈-SH, DMPA, CHCl₃: TFT = 1:3, UV 365 nm irradiation, 30 minutes, r.t., 65%; (ii) 4-oxo-4-(prop-2-yn-1-yloxy) butanoic acid, DMAP, DIPC, CH₂Cl₂: TFT = 1:3, r.t., 72%.

Figure 2. Synthetic route toward alkyne functionalized flourinated POSS (FPOSS-alkyne)

¹H NMR spectroscopy was utilized to monitor the progress of “thiol-ene” reaction between VPOSS-OH and F₈-SH, and the reaction was found to complete within 30 minutes. No precipitation was observed during the irradiation. After the “thiol-ene” reaction, ¹H NMR spectra in Figures 1b show that the resonance peaks corresponding to the vinyl groups on VPOSS-OH at 6 6.00 ppm disappears completely, indicating that all the vinyl groups have been coupled with the F₈ chains. New resonances appear at 6 2.5-2.8 and 2.2-2.4 ppm, and can be assigned to the protons on the methylene group adjacent...
to the sulfur (protons $d$ and $e$) and to the -CF$_2$- (proton $f$), respectively. The integral ratio among the peaks of $a$, $d + e$, and $f$ is 2:29:15, close to the proposed structure (2:28:14), confirming the quantitative functionalization.

More convincing evidence was obtained from MALDI-TOF mass spectroscopy, and the results are shown in Figure 2a. A single peak with a molecular weight of 4033.04 Da is found. This is in good accordance with the calculated molecular weight, 4032.83 Da ($[\text{C}_{86}\text{H}_{61}\text{F}_{119}\text{O}_{13}\text{S}_7\text{Si}_8\text{Na}]^+]$). No other peaks are observed, indicating the success and completion of the reaction.
Further esterification with 4-oxo-4-(prop-2-yn-1-yloxy) butanoic acid attaches an alkyne functionality on the FPOSS. To obtain a homogeneous mixture for reaction, a mixed solvent of TFT and anhydrous CH$_2$Cl$_2$ is chosen. $^1$H NMR spectrum shows that the resonance at $\delta$ 3.8 ppm corresponding to protons on the methylene adjacent to the
hydroxyl group (proton $a$) shifts completely to $\delta$ 4.2 ppm after the formation of the ester group, confirming a quantitative installation of alkyne functionality onto the FPOSS. The resonance of proton on the alkyne (proton $t$) can be identified at $\delta$ 2.4 ppm, while protons on the methylene adjacent to the alkyne (proton $s$) at $\delta$ 4.7 ppm. The MALDI-TOF mass spectroscopy result provides unambiguous evidence of the success of the esterification. The observed molecular weight is 4171.39 Da while the calculated molecular weight is 4170.87 Da ([C$_{93}$H$_{67}$F$_{119}$O$_{16}$Si$_8$Na]$^+$), revealing the preciseness of the product (Figure 2b).
Figure 4. MALDI-TOF mass spectra of FPOSS-OH (a) and FPOSS-alkyne (b)
5.2 “Clicking” FPOSS onto Polystyrene: A Model Reaction

Copper catalyzed Huisgen [3+2] cycloaddition (CuAAC) has been widely applied to synthesize polymers with a variety of architectures under mild conditions.\textsuperscript{32,33} The high efficiency of this type of “click” chemistry guarantees a quantitative reaction even though the chain-end reactivity of polymers (such as azides) is usually reduced. Complicated purification procedures such as fractionation can thus be avoided. Here we take “clicking” FPOSS-alkyne onto PS-N\textsubscript{3} as a model reaction to testify the chemical feasibility and technical simplicity of our strategy. Azide functionalized PS (PS-N\textsubscript{3}) with various molecular weights are prepared using atomic transfer radical polymerization (ATRP) followed by nucleophilic substitution with sodium azide.\textsuperscript{36} The synthetic route toward FPOSS-PS conjugates is shown in Scheme 3.

\begin{equation}
\begin{array}{c}
\text{Reagents and Conditions: (i) CuBr, PMDETA, TFT, r.t., 72\%.}
\end{array}
\end{equation}

Figure 5. Synthetic route of FPOSS-PS via “click” reaction

A fluorous solvent TFT is used to increase the solubility of FPOSS-alkyne. A slight excess of PS-N\textsubscript{3} was added to fully consume the FPOSS-alkyne. After purification with silica column, the product shows no trace of the azide adsorption peak (\textasciitilde 2100 cm\textsuperscript{-1}) in the FT-IR spectrum (Figure S1 in ESI). A new adsorption at \textasciitilde 1670 cm\textsuperscript{-1} corresponding to the carbonyl group is observed due to the incorporation of FPOSS (Figure S1 in ESI).
In $^1$H NMR spectrum, both the resonance peaks representing FPOSS and PS moieties can be clearly identified (Figure 3). Specifically, the resonances at $\delta$ 2.3-2.5 and 2.6-2.8 ppm correspond to the fluoroalkyl chains on FPOSS (protons $n$, $r$, and $s$), while the resonances between $\delta$ 6.3-7.0 ppm can be assigned to the aromatic protons on PS (proton $f$). The covalent connection is also confirmed by the emergence of the resonances at $\delta$ 5.2 ppm, which are attributed to the protons adjacent to newly formed triazole ring (protons $g$ and $v$). A narrow molecular weight distribution of the FPOSS-PS compound can be identified by SEC chromatography. Its retention volume is shifted to a lower value as compared to its precursor, PS-N$_3$ (Figure 4).

![Figure 6. $^1$H NMR spectra of FPOSS-PS. The results were based on the sample FPOSS-PS$_{24}$](image)
MALDI-TOF mass spectroscopy provides further evidence to prove the success of this model reaction. A single narrow distribution with molecular weights in accordance to the proposed structure is observed (Figure 5). A representative mono-isotopic peak with $m/z = 5869.17$ Da is very close to the calculated molecular mass for a 14-mer (5868.71 Da, $[\text{C}_{211}\text{H}_{190}\text{F}_{119}\text{N}_{3}\text{O}_{18}\text{S}_{7}\text{Si}_{8}\text{Ag}]^+$). The difference between two neighboring peaks is 104.06 Da, corresponding to the mass of one styrene repeating unit. All these molecular characterizations clearly confirm the success of this model reaction. The detailed molecular characterization data are summarized in Table 1.
Figure 8. MALDI-TOF mass spectrum of FPOSS-PS. The results were based on the sample FPOSS-PS$_{24}$
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<th>$M_n^{PS}$</th>
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<th>$PDI$</th>
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$^a$ Overall molecular weight; $^b$ Molecular weight of PEO, calculated based on $^1$H NMR; $^c$ Molecular weight of PS, calculated based on $^1$H NMR; $^d$ Number of FPOSS per polymer chain, calculated based on $^1$H NMR (see Eq. S1, S2, and S3 in ESI); $^e$ Molecular weight distribution measured by SEC; $^f$ weight percentage of FPOSS.

Figure 9. Molecular Characterization of FPOSS-containing Polymers
5.3 Tethering Multiple FPOSS Units onto a Polystyrene Chain

Increasing the fluoro content in materials by attaching multiple fluorous clusters is especially critical to enhance the surface property. In this section, we try to demonstrate the installation of multiple FPOSS nanoparticles onto a single polymer chain. The synthetic route is illustrated in Scheme 4. To prepare PS with multiple reactive azide functionalities along the polymer chain, 4-vinyl benzyl chloride is co-polymerized with styrene using RAFT polymerization, followed by nucleophilic substitution with sodium azide. The FPOSS is then installed via the CuAAC “click” reaction.

Scheme 4. Synthetic route of PS/FPOSS via “click” reaction

Reagents and Conditions: (i) AIBN, toluene, styrene, VBC, 110 °C, 24 h, 41%; (ii) NaN₃, DMF, 24h, r.t., 80%; (iii) CuBr, PMDETA, TFT, 24h, r.t., 71%.

Figure 10. Synthetic route of PS/FPOSS via “click” reaction
The RAFT polymerization was carried out with ETC as the chain transfer agent and AIBN as the initiator. The conversion was kept below 50% to maintain a narrow molecular weight distribution. The overall molecular weight was controlled by polymerization time while the average number of VBC repeating unit per polymer chain was adjusted through the feed ratio of two monomers. This number can be determined based on the $^1$H NMR result by the ratio between the integrated resonance peaks corresponding to the protons on the methylene groups adjacent to the chloride (4.51 ppm, proton b in Figure 6a) and the protons on the phenyl ring (6.30-7.40 ppm) (Eq. S1, see ESI for detailed calculation). The overall molecular weight is calculated based the PS standard calibration. A narrow distribution is observed in the SEC chromatograph with PDI = 1.03 (Figure 7, red).
Figure 11. $^1$H NMR spectra of PS/Cl (a), PS/N$_3$ (b), and PS/FPOSS (c). The results were based on the sample PS$_{230}$/FPOSS$_{10}$.

The chloro groups along the PS chain can be readily converted to azide functionality by treating with sodium azide in DMF. Typical azide absorption is found in FT-IR spectrum at 2100 cm$^{-1}$ with a relatively strong intensity due to multiple azides per chain (Figure S2 in ESI). $^1$H NMR spectrum shows a complete resonance shift from $\delta$ 4.5 ppm.
to δ 4.3 ppm (proton b), indicating that all the chloride groups have been converted to the azide groups.

Figure 12. SEC chromatography of PS/Cl (red) and PS/FPOSS (blue). The results were based on the sample PS230/FPOSS10 with overall PS number average molecular weight of 23,000 g/mol and FPOSS number per chain of 10

FPOSS can be readily attached onto PS/N₃ via “click” chemistry with high efficiency under mild conditions. In this case, excess FPOSS-alkyne is added to ensure all the azide groups are consumed. No residual adsorption peak at 2100 cm⁻¹ in the FT-IR spectrum was observed after the reaction (Figure S2 in ESI). The SEC chromatograph shifts to a much lower retention volume, indicating an increase of the hydrodynamic volume due to incorporation of multiple FPOSSs (Figure 7, blue). In ¹H NMR spectrum, resonance from the FPOSS moiety can be clearly identified (Figure 6c). The broad chemical shifts at δ 2.7 ppm (protons g and h) and δ 2.3 ppm (proton k) are assigned to the protons on the
methylene adjacent to the sulfur and -CF₂- group, respectively. The solubility of the product in common solvents is greatly enhanced. They can now be reversibly dissolved in most common organic solvents such as toluene, THF, CHCl₃, CH₂Cl₂, and others, even after long-term storage. The detailed molecular characterization data are also summarized in Table 1.

5.4 Giant Surfactants Based on FPOSS and Diblock Copolymer

In addition to several metastable phases, various thermodynamically stable phase morphologies, including lamellae (Lam), bicontinuous double gyroids (DG), hexagonal packed cylinders (Hex), and body-centred cubic packed spheres (BCC), have been observed in diblock copolymers with chemically distinct components. Adding an additional block will greatly expand the scope of assembled structures. Incorporation of a “third” phase into amphiphilic diblock polymers, such as PS-b-PEO, will generate “triblock copolymer-like” giant surfactants with multiple interactions. This class of materials may expand the utility of block polymers and render them with novel self-assemble behaviors. FPOSS could be an ideal candidate due to its precisely defined chemical structure and high immiscibility to both blocks.

Following a similar approach, we then extend our study to FPOSS-containing diblock copolymers. With proper design and synthesis of block polymer precursors with an azide functional group at specific location, FPOSS can be precisely fixed at the chain end
(FPOSS-PS-b-PEO), or at the junction point [PS-(FPOSS)-PEO] (Scheme 1). The synthetic route was outlined in Figure 13.

Figure 13. Synthetic route of giant surfactants based on FPOSS and PS-b-PEO diblock copolymer

Reagents and Conditions: (i) CuBr, PMDETA, TFT, r.t., 71%; (ii) CuBr, PMDETA, TFT, r.t., 75%.
As the first evidence of the success of this click reaction, the typical azide absorption bands at $\sim 2100 \text{ cm}^{-1}$ in FT-IR spectra of both FPOSS-PS-b-PEO and PS-(FPOSS)-PEO disappear completely (Figure S3 in ESI). In the $^1$H NMR spectra, the signals...
corresponding to the FPOSS component at $\delta$ 2.7 ppm and $\delta$ 2.3 ppm can be clearly observed (Figures 8a and 8b). Detailed assignment can be found in Figure 8. The degree of functionality can be estimated based on the integrated peak area of the proton on the phenyl groups ($\delta$ 6.2-7.2 ppm, proton $g$) and the protons on the fluroalkyl chains ($\delta$ 2.5-2.8 ppm, proton $n$, $p$, and $s$) (Eq. S2, See ESI for detailed calculation). In both case, the calculations indicate quantitative functionality. In the SEC chromatogram, a clear shift to a low retention volume can be found after the incorporation of FPOSS, due to the increase of hydrodynamic volume (Figure 9, blue). Both SEC chromatograms are narrow and symmetric, confirming the well-defined structures.
Figure 15. SEC chromatography of PEO-b-PS-N3 (a, red), FPOSS-PS-b-PEO (a, blue), PS-(N3)-PEO (b, red), and PS-(FPOSS)-PEO (b, blue). The results were based on the sample FPOSS-PS28-b-PEO45 and PS52-(FPOSS)-PEO45, respectively.
CHAPTER VI

CONCLUSION

In summary, a novel functionalized FPOSS, FPOSS-alkyne, with seven perfluorinated alkyl chains and one alkyne group was synthesized and used as a versatile building block to introduce fluorous molecular clusters into other materials. Based on this, CuAAC “click” chemistry provides an efficient and modular approach to construct FPOSS-containing polymers with various architectures and quantitative functionality. FPOSS can be tethered onto either PS or PS-\(b\)-PEO at precise locations, including chain end (FPOSS-PS, FPOSS-PS-\(b\)-PEO), the junction point [PS-(FPOSS)-PEO], or randomly along the polymer chain (PS/FPOSS). Incorporation of the “third” fluorous phase will greatly expand the scope and utility of polymers. These FPOSS-containing polymers having precisely defined topologies can serve as model compounds to study their novel self assembly behaviors in the bulk, solution, and thin film states.
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