T₁₀ Polyhedral Oligomeric Silsesquioxane-Based Shape Amphiphiles with Diverse Head Functionalities via "Click" Chemistry

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ⓢ *Supporting Information*

ABSTRACT: Head diversification of shape amphiphiles not only broadens the scope of supramolecular engineering for new self-organizing materials but also facilitates their potential applications in high technologies. In this letter, T₁₀ azido-functionalized polyhedral oligomeric silsesquioxane (POSS) nanoparticle was used to construct new shape amphiphiles via sequential "click" chemistry for addressing two issues: (1) new symmetry of T₁₀ POSS head could enrich the self-assembly behaviors of shape amphiphiles, and (2) copper-catalyzed azide–alkyne cycloaddition (CuAAC)-based head functionalization strategy allows the introduction of diverse functionalities onto POSS heads, including bulky ligands (i.e., isobutyl POSS) and UV-attenuating ones (i.e., ferrocene and 4-cyano-4′-biphenyl). This study expands the library of POSS-based shape amphiphiles with numerous possibilities for head manipulations, offering an important step toward new shape amphiphiles beyond traditional hydrophobic/hydrophilic nature for potential applications in giant molecule-based nanoscience and technology.

F₁ = Bulky Ligands, such as BPOSS...
F₂ = UV-Attenuating Ligands, such as ferrocene, liquid crystal...
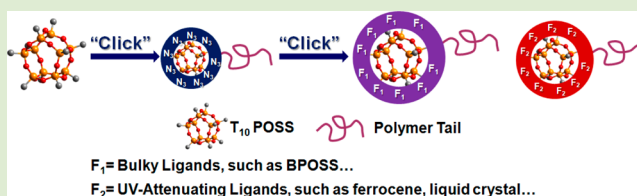
Fabrication of functional and robust nanomaterials by lithographic techniques has been progressively developed to such a degree that practically, this approach has been widely utilized in different industrial applications.[1] With the increasing resolution required on nanopatterning in microelectronic industry, a combined approach of lithography and self-assembly of soft materials is paving the new path entering nanoscience and nanotechnology.[2] For example, the sophisticated practices of self-organizing materials, including liquid crystals,[3] amphiphilic block copolymers,[4] small-molecule surfactants and lipids,[5] and giant molecules,[6] may hold the promises in generating new structures and devices with feature sizes of several nanometers, especially in the sub-10 nm scale.[7]

Giant molecules generally describe precisely defined macromolecules constituted of molecular nanoparticle (MNP) subunits or its conjugates with other building blocks.[6] As a subclass of giant molecules, shape amphiphiles are usually built upon molecular segments of distinct shapes and competing interactions.[6] Among them, MNPs tethered with polymers represent a typical class of shape amphiphiles, which provides a versatile platform to engineer nanostructures with sub-10 nm feature sizes.[6] In recent years, various functional MNPs have been employed as "head" of shape amphiphiles to connect with soft polymeric tails, including global protein,[8] polyoxometalate (POM),[9] fullerene,[10] and polyhedral oligomeric silsesquioxane (POSS).[11,12] Among them, POSS is of particularly interest due to its precisely defined rigid structures and rich surface

chemistry.[13−19] Significant advances in T₈ vinyl POSS (VPOSS)−polymer conjugates have enabled the precision synthesis of a library of POSS-based shape amphiphiles with well-controlled chemical compositions and macromolecular architectures.[20−23] It was found that the self-assembly behaviors of shape amphiphiles are intimately dependent on their primary chemical structures, such as topological variation.[24] A typical example is the different self-assembly behaviors of topological isomeric shape amphiphiles that possess an identical volume fraction of hydrophobic tails but distinct polymer topologies in the bulk.[7] For example, DPOSS-PS₃₅ consisting of one dihydroxyl-functionalized POSS head tethered with one hydrophobic polystyrene tail could self-organize into a double gyroid structure, while DPOSS-2PS₁₇ with two PS tails formed a hexagonally packed cylinder structure.[7]

In addition, the head nature of shape amphiphiles also represents another important parameter to tune their self-assembly behaviors.[7,24] First, head symmetry could strongly affect the packing behavior of heads that may further influence the self-organization of a whole macromolecule. For example, a recent computer simulation work has revealed that the supramolecular structure of shape amphiphile could change

Scheme 1. Synthetic Route for Shape Amphiphiles Using Sequential "Click" Chemistry[a]
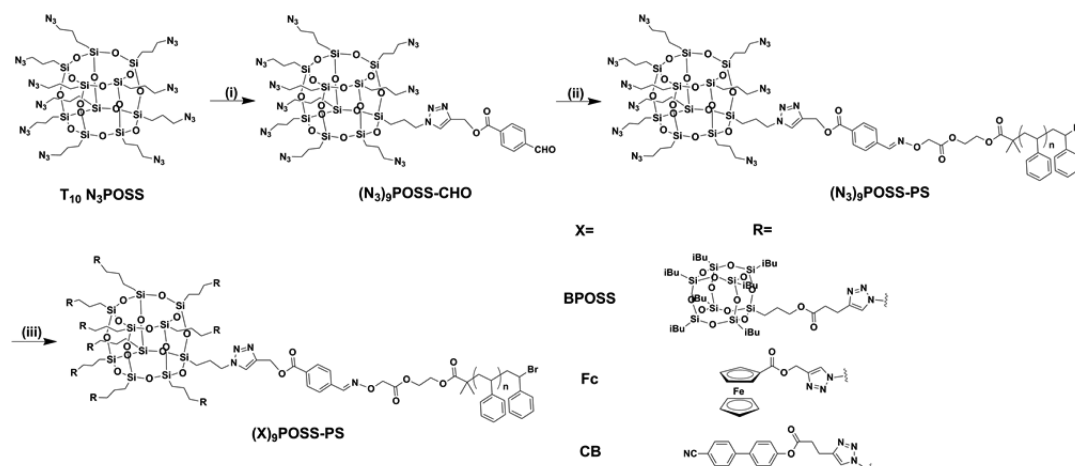
[a]Reagents and conditions: (i) Prop-2-yn-1-yl 4-formylbenzoate, CuBr, PMDETA, toluene, 25 °C, 32%; (ii) NH$_2$O-PS, TsOH, THF, 25 °C, 68%; (iii) BPOSS-alkyne or ferrocene-alkyne or 4-cyano-4′-biphenyl-alkyne, CuBr, PMDETA, THF, 25 °C, 83% for (BPOSS)$_9$POSS−PS, 79% for (Fc)$_9$POSS−PS, and 78% for (CB)$_9$POSS−PS.
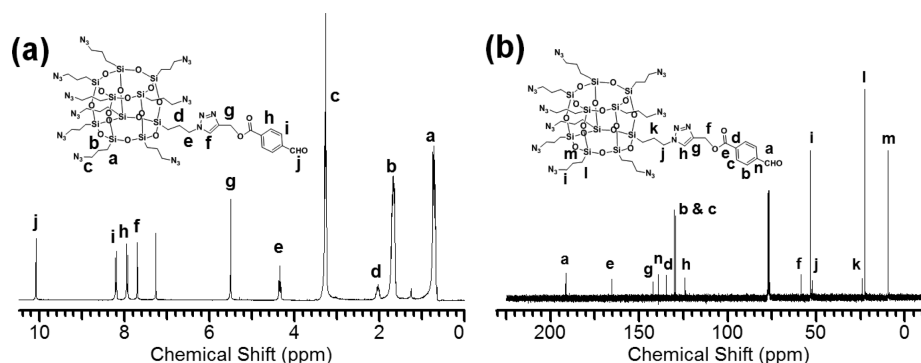

Figure 1. ^{1}H NMR (a) and ^{13}C NMR (b) spectrum of (N$_3$)$_9$POSS-CHO.

from a bilayer sheet to hexagonal packing as its cubic headgroup becomes a rod one with the same volume.[24,25] Second, fine-tuning the head volume by modifying the head with ligands of different sizes provides a straightforward way to adjust the volume fraction between heads and tails of giant molecules and thus, results in different phase structures. Notably, a shape amphiphile with a very big head consisted of three DPOSS cages and a short PS tail might even induce an inverse phase structure.[7] Third, tailoring the interaction among heads by varying the number and strength of surface functionalities could potentially influence the multivalent effects of shape amphiphiles.[26] Finally, the introduction of stimuli-responsive (such as redox, magnetic, or electro-responsive) functionalities onto the POSS head could generate a new class of shape amphiphiles beyond the traditional hydrophobic/hydrophilic nature, which may allow a broader guidance of packing behaviors and a wider range of potential applications under different force fields.[24] The core issue of all these aspects is critically dependent on the nature of POSS heads and their related functionalization strategy. In order to accommodate those bulky and responsive functional ligands, it is necessary to develop new nanobuilding blocks other than T$_8$ VPOSS to be the head scaffold of shape amphiphiles with corresponding efficient and robust chemical ligations.

To address this issue, deca(3-azidopropyl)silsesquioxane (T$_{10}$ N$_3$POSS)[27] with 10 azido functional groups on the surface was

selected as a new candidate of head scaffolds for shape amphiphiles. It is the major product (∼50%) from the azidation of chloro-functionalized POSS (ClPOSS).[27] T$_{10}$ POSS possesses distinct molecular symmetry (D_{5h} symmetry) compared with T$_8$ POSS (O_h symmetry).[28] It expands the scope of head diversification of shape amphiphiles by offering new symmetry, denser surface functionalities, and a novel head modification approach based on copper-catalyzed azide−alkyne cycloaddition (CuAAC) "click" chemistry, which has been demonstrated as a powerful method for modification of N$_3$POSS.[27,29] In particular, CuAAC reaction is suitable for N$_3$POSS head modifications with various functionalities including bulky ligands or UV attenuating functionalities, which cannot be perfectly achieved by using thiol−ene functionalization of the VPOSS cage.[30,31]

In this letter, we strive to develop a new family of shape amphiphiles with a T$_{10}$ N$_3$POSS cage as the head using sequential "click" strategy. The study on the use of CuAAC for diverse POSS head functionalization with bulky functionalities (i.e., BPOSS) and stimuli responsive ones (i.e., ferrocene and 4-cyano-4′-biphenyl; Scheme 1) has been systematically performed. In such a way, we aim to establish a novel and general method to construct shape amphiphiles with diverse head surface chemistry and found the first step for developing new shape amphiphiles beyond the traditional hydrophobic/

hydrophilic nature for new potential applications in high technologies.

The N_3POSS is generally prepared by the azidation of the ClPOSS cage, which is obtained through the hydrolytic condensation reaction of 3-chloropropyltrimethoxysilane[27] and has been regarded as a versatile nanobuilding block toward different hybrid materials.[32,33] Due to the cage rearrangement under severer conditions during azidation, the resulting N_3POSS crude product usually contains a mixture of T_8, T_{10}, and T_{12} POSS cages.[27] The desired T_{10} N_3POSS can be further isolated by a chromatographic method with a yield of 45%.[27]

Recently, "click" chemistry has provided a facile, versatile, and robust way to generate a large variety of monofunctionalized "clickable" building blocks.[34,35] For example, Chiara et al. have employed stoichiometry-controlled CuAAC surface modification of T_8 N_3POSS to prepare a series of monofunctionalized T_8 N_3POSS derivatives.[35] This method can also be applicable to the synthesis of monofunctionalized T_{10} N_3POSS. Under the established experimental condition,[35] an equal molar mixture of T_{10} N_3POSS and prop-2-yn-1-yl-4-formylbenzoate (see SI) were fully dissolved in toluene. After 1 day, all alkyne ligands have been fully reacted and the targeted monoadduct could be easily isolated by chromatographic method as colorless oil from the crude products with a yield of ~30%. This result is consistent with many previous reported work.[34,35] The successful synthesis of the $(N_3)_9POSS$-CHO was fully supported by NMR techniques. For example, the characteristic chemical shift at δ 10.09 ppm (^{1}H NMR, Figure 1a) as well as the one at δ 191.43 ppm (^{13}C NMR, Figure 1b) suggested that the aldehyde group had been successfully installed onto N_3POSS surface. The integration ratio between protons b to protons d or the ratio between protons c to protons e was about 9:1 (Figure 1a). Notably, the presence of one aldehyde group in $(N_3)_9POSS$-CHO can be further employed to conjugate with a polymer tail using oxime ligation,[36] while nine azido groups on POSS periphery are ready for head diversification by using different alkyne-functionalized ligands via CuAAC "click" reaction. The possibility to do the sequential "click" reactions greatly expands the scope of T_{10} POSS-based shape amphiphiles with diverse head functionalities.

Oxime ligation, which is a highly reactive, and bio-orthogonal "click" reaction,[37] was then used for the conjugation reaction between amino-oxy chain-end functionalized polymer (NH_2O-PS) and $(N_3)_9POSS$-CHO to afford a shape amphiphile precursor, $(N_3)_9POSS$-PS. The product was fully characterized by ^{1}H NMR (Figures 2a and S1a), ^{13}C NMR (Figures S2a and S1b), FT-IR (Figure S3a), and SEC (Figure 3). First, the disappearance of aldehyde proton chemical shift at δ 10.09 ppm in ^{1}H NMR spectrum (Figure S1a) demonstrated the near quantitative reaction, which is in accordance with the missing of related carbon chemical shift at δ 191.43 ppm in ^{13}C NMR result (Figure S1b). In addition, the intact multiple azido groups and POSS cage were further confirmed by the observation of a strong vibrational band at ~2100 cm^{-1} and another vibrational band at ~1120 cm^{-1} in the FT-IR spectrum (Figure S3a), respectively. Finally, the SEC profile of $(N_3)_9POSS$-PS (M_n = 5.6 kg/mol, PDI = 1.04, Table 1; Figure 3) exhibits a monomodal, symmetric peak, shifted to a lower retention volume relative to that of NH_2O-PS (M_n = 4.8 kg/mol, PDI = 1.12) due to an increase of molecular mass of N_3POSS head. Therefore, all the evidence fully support the molecular structure and purity of $(N_3)_9POSS$-PS.
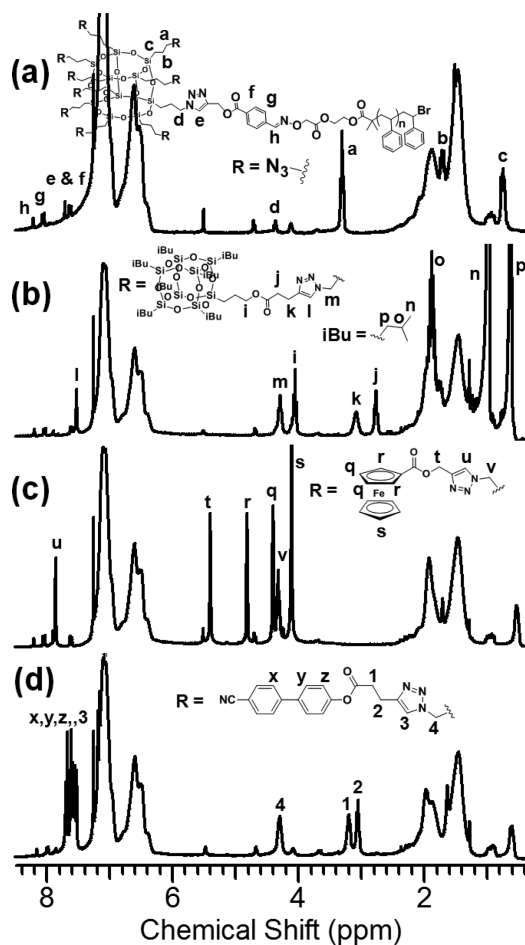

Figure 2. ^{1}H NMR spectra of (a) $(N_3)_9POSS$−PS, (b) $(BPOSS)_9POSS$−PS, (c) $(Fc)_9POSS$−PS, and (d) $(CB)_9POSS$−PS.
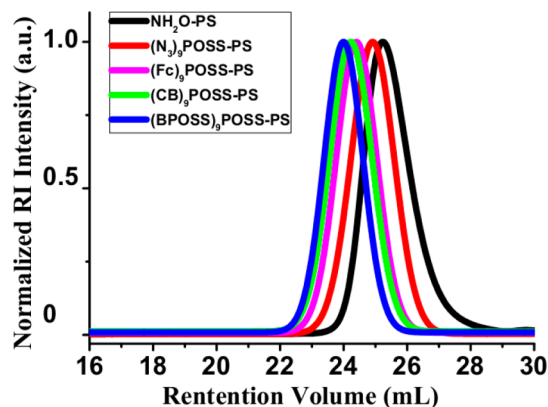

Figure 3. SEC overlay of NH_2O-PS (black curve), $(N_3)_9POSS$−PS (red curve), $(Fc)_9POSS$−PS (pink curve), $(CB)_9POSS$−PS (green curve), and $(BPOSS)_9POSS$−PS (blue curve).

To test the efficiency and versatility of CuAAC for diverse head functionalization of macromolecular precursor, three kinds of functional ligands (BPOSS-alkyne, ferrocene-alkyne, and 4-cyano-4′-biphenyl-alkyne) were used to react with the $(N_3)_9POSS$-PS. BPOSS moiety was employed as the first model ligand due to its relatively large molecular size. In general, block copolymers containing multiple BPOSS units have been attracting people's attentions since they can further self-organize into different supramolecular hierarchical struc-

Table 1. Summary of Molecular Weight Characterizations[⊥]

sample	molecular formula (a)	M (calcd)(b)(Da)	m/z (obs)(c)	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI
$(N_3)_9POSS-PS$				6.0k	5.6k	1.04
$(BPOSS)_9POSS-PS$	$[C_{662}H_{1036}AgN_{31}O_{148}BrSi_{82}]^+$	14286.1	14285.5	14.6k	13.8k	1.02
$(Fc)_9POSS-PS$	$[C_{464}H_{478}AgN_{31}O_{40}BrFe_9Si_{10}]^+$	8098.6	8098.0	8.4k	7.7k	1.02
$(CB)_9POSS-PS$	$[C_{500}H_{487}AgN_{40}O_{40}BrSi_{10}]^+$	8163.4	8162.8	8.4k	8.1k	1.03

[⊥]The molecular formula (a), the calculated molecular weights (b), and the experimentally observed m/z (c) from linear mode are based on 35-mer of $(BPOSS)_9POSS-PS$, $(Fc)_9POSS-PS$ and $(CB)_9POSS-PS$ with a silver cation ($[M·Ag]^+$).

tures due to strong phase separation between BPOSS domains and polymer domains (i.e., PS).[38−40] Therefore, the facile and precise construction of shape amphiphiles with multiple BPOSS cages modified head is highly desired. To achieve this, thiol−ene reaction between VPOSS-PS and PSS-(3-Mercapto)propyl-heptaisobutyl substituted (BPOSS-SH) was first attempted (Scheme S1). However, it was found that thiol−ene reaction could not afford the complete installation of BPOSS-SH onto the VPOSS-PS precursor. Only ∼60% of vinyl groups on the VPOSS of VPOSS-PS precursor were consumed after 2 h thiol−ene reaction (Figure S4b). And this result cannot be further improved significantly by longer reaction time or higher concentrations of functional thiol and photoinitiator. This is because the steric effect would decrease the efficiency of addition of bulky ligand onto VPOSS cage by thiol−ene reaction.[34] Alternatively, the newly prepared $(N_3)_9POSS-PS$ precursor provides a possible way for full incorporation of BPOSS units onto the POSS head by CuAAC reaction.

The complete head functionalization was confirmed by the disappearance of a resonance chemical shift at δ 3.30 ppm in ^{1}H NMR spectrum (Figure 2b) as well as the chemical shift at δ 53.52 ppm in ^{13}C NMR spectrum (Figure S2b), which corresponds to the methylene near the azido group. This perfectly matches with the result obtained from FT-IR spectrum (Figure S3b). No band at ∼2100 cm^{−1} characteristic of the azido group can be observed. In addition, the formation of triazole was proven by the occurrence of new resonance chemical shift at δ 4.28 ppm, which was originally at δ 3.30 ppm (^{1}H NMR, Figure 2b). The precisely defined macromolecular structure was further demonstrated by the MALDI-TOF mass spectrum (Figure 4a), which was obtained under the positive linear mode due to the relatively high molecular weight of the product. It shows a narrow distribution with molecular weights in accordance to the proposed structure. A representative mass peak at m/z 14285.5 for $(BPOSS)_9POSS-PS$ is in close match with the calculated average molecular mass of 14286.1 Da for 35-mer with a silver ion. The SEC diagram of $(BPOSS)_9POSS-PS$ (M_n = 13.8 kg/mol, PDI = 1.02, Table 1; Figure 3) shows a monomodal symmetric peak at a lower retention volume than that of $(N_3)_9POSS-PS$ due to the incorporation of nine BPOSSs. The successful synthesis of $(BPOSS)_9POSS-PS$ has demonstrated that CuAAC is an ideal tool for installing bulky functional moieties onto the N3POSS head of shape amphiphile precursor.

Besides BPOSS, to further test the versatility of this new system and develop the family of shape amphiphiles, stimuli-responsive functionalities (ferrocene and 4-cyano-4′-biphenyl) were then employed. Herein, both of two ligands are UV-attenuating ones which cannot be completely installed onto the head of VPOSS-PS system by thiol−ene reaction. It is because they may absorb UV-light of similar wavelength as the photoinitiator to sacrifice the efficiency of thiol−ene reaction.[41] In this work, the shape amphiphiles precursor (($N_3)_9POSS-$
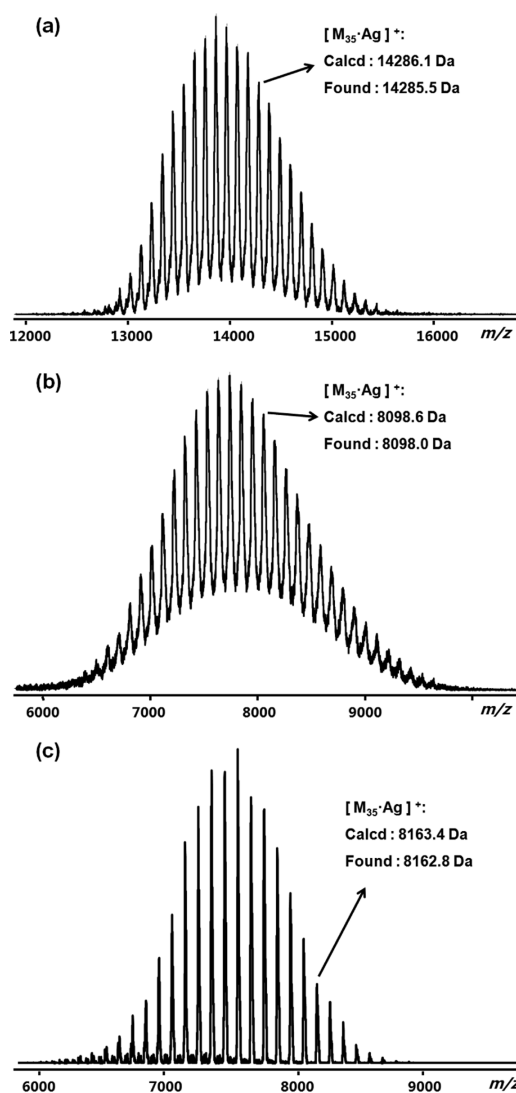
Figure 4. MALDI-TOF mass spectra of (a) $(BPOSS)_9POSS-PS$, (b) $(Fc)_9POSS-PS$, and (c) $(CB)_9POSS-PS$. The full spectrum was obtained in positive linear mode.

PS) was fully modified using ferrocene and 4-cyano-4′-biphenyl by CuAAC "click" chemistry.

Ferrocene is considered as an important material in a wide range of applications from fuel additive, pharmacy to catalyst.[42] The introduction of ferrocene units into block polymers has shown interesting self-assembly behaviors.[43,44] Moreover, ferrocene can be easily oxidized to be an ferrocenium ion $[(\eta^5-C_5H_5)_2Fe^{III}]^+$, enabling the redox responsive behaviors of whole molecules.[45,46] Again, the targeted product was first tried by thiol−ene head functionalization of VPOSS-PS with ferrocene thiol. The reaction efficiency is quite low (with only ∼20% vinyl groups was reacted (Figure S4c) since

ferrocene shares the similar absorbing wavelength with the photoinitiator as described above.[34,41]

Alternatively, ferrocene unit can be successfully installed onto head of $(N_3)_9$POSS−PS using CuAAC reaction. The successful surface functionalization was also supported by the complete disappearance of proton chemical shift at δ 3.30 ppm and the appearance of proton chemical shift at δ 4.28 ppm as discussed above (Figure 2c). Similarly, in ^{13}C NMR spectrum (Figure S2c), no chemical shift corresponding to the -CH$_2$N$_3$ at δ 53.52 ppm was observed. The intact of POSS cage was confirmed by the observation of a single peak at δ −69.42 ppm in the ^{29}Si NMR spectrum (Figure S5). Additionally, FT-IR spectrum (Figure S3c) with no azido band at ~2100 cm^{-1} provides further evidence for the complete functionalization. Furthermore, a monomodal symmetric peak (M_n = 7.7 kg/mol, PDI = 1.02, Table 1) at a lower retention volume than that of $(N_3)_9$POSS−PS in the SEC overlays (Figure 3), and one narrow molecular weights distribution with a representative mass peak at m/z 8098.0 for $(Fc)_9$POSS−PS$_{35}$ (Ag$^+$ adduct; calculated 8098.6 Da) in MALDI-TOF mass spectrum (Figure 4b) were both observed, which indicate the successful synthesis of final product. The POSS head fully coated with ferrocene units would transform magnetic property onto related shape amphiphiles.[47]

Liquid crystal molecules are anisotropic materials that exhibit a mesophase intermediate between the disordered liquid phase and ordered solid phase, which play an important role in material science and engineering.[48] A cluster of mesogens will lead to intriguing phase behaviors. For example, an isotropic molecule based on fullerene tethered with 12 cyanobiphenyl groups exhibit a smectic phase.[49] The corporation of liquid crystal molecules onto POSS cages also offers new opportunities to tailor the molecular packing of POSS cages and generate hierarchical structures.[50−53] Moreover, the assembly behavior of liquid crystal molecule modified materials can be guided by output magnetic field.[54] However, many typical liquid crystal moieties (i.e., 4-cyano-4′-biphenyl) are also UV-attenuating which cannot be fully installed on the POSS head by thiol−ene modification of VPOSS-PS (only ~30% vinyl groups were reacted when cyanobiphenyl thiol (CB-SH) was used, see Figure S4d). Herein, CuAAC was again used to do the complete head modification of $(N_3)_9$POSS−PS with 4-cyano-4′-biphenyl-alkyne to develop shape amphiphiles with optical properties.[55]

Similar to $(Fc)_9$POSS−PS, the macromolecular structure of $(CB)_9$POSS−PS was again fully supported by ^{1}H NMR (the disappearance of chemical shift at δ 3.30 ppm, Figure 2d), ^{13}C NMR spectrum (the disappearance of chemical shift at δ 53.52 ppm, Figure S2d), and FT-IR spectrum (the disappearance of the vibrational band at ~2100 cm^{-1}, Figure S3d). In addition, the SEC overlay (Figure 3) reveals a decreased retention volume of $(CB)_9$POSS−PS relative to $(N_3)_9$POSS−PS (M_n = 8.1 kg/mol, PDI = 1.03, Table 1). The most striking evidence comes from the MALDI−TOF mass spectrum as shown in Figure 4c. One symmetric distribution of molecular weights is observed under the positive linear mode, where the mass of each peak matches perfectly with that expected for the proposed structure (e.g., for 35-mer with the formula of $[C_{500}H_{487}AgN_{40}O_{40}BrSi_{10}]^+$, observed m/z 8162.8 Da vs calcd 8163.4 Da). Therefore, it can be concluded that $(CB)_9$POSS−PS was also successfully synthesized from the macromolecular precursor using CuAAC "click" head functionalization approach.

In summary, the scope of shape amphiphiles with head diversification has been widely extended by the use of T_{10} N$_3$POSS as the head and CuAAC as the head functionalization method. T_{10} N$_3$POSS offers several advantages in the preparation of shape amphiphiles, including a new symmetry of the head, a denser cluster of functional groups, etc. The CuAAC "click" head functionalization method is quite efficient and versatile, allowing the introduction of a broad range of functionalities onto shape amphiphiles, including BPOSS, ferrocene and 4-cyano-4′-biphenyl. The versatile T_{10} N$_3$POSS nanobuilding block and CuAAC head modification strategy provide numerous opportunities to construct the first generation of stimuli responsive shape amphiphiles.[56] Relevant research work is ongoing in our laboratory to investigate the self-assembly behaviors of these shape amphiphiles and reveal the underlying physical properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on the synthesis and characterization of the compounds. 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.

■ ACKNOWLEDGMENTS

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