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Polyhedral oligomeric silsesquioxane meets “click” chemistry: Rational design and facile preparation of functional hybrid materials

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For the occasion of 70th birthday of Professor Axel H. E. Müller for his pioneering contribution in polymer chemistry.

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ABSTRACT

The continuous demand for novel hybrid materials in specific technological applications inspires people to develop new synthetic strategies in a modular and efficient way. In the recent years, extensive efforts have been devoted to using polyhedral oligomeric silsesquioxane (POSS) to construct multifunctional nanohybrids and nanocomposites with tunable hierarchical structures and unparalleled properties. The shape-persistent nanostructure and diverse surface chemistry make those nanocaged materials ideal building blocks for such purposes. Functionalization of POSS cages are further facilitated by the introduction of “click” chemistry at the beginning of this century. “Click” reactions include several kinds of selective and orthogonal chemical ligations with high efficiency under mild reaction conditions. The concept has generated real stimulus not only in elegantly preparing materials of choice, but in making the leap from laboratory to industrial scale-up of POSS-based hybrid materials as well.

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1. Introduction

Successful molecular design, synthesis and fabrication of functional soft hybrid materials with explicit properties for specific applications have been a long-lasting goal for scientists and engineers. A classical way for chemists frequently used is the "trial-and-error" approach. By design and synthesis of a series of polymeric materials with systematic variation in primary chemical structures including functional groups, macromolecular architectures, molecular weights and others, people aim to establish structure-property relationships for further optimization of their property and performance. It is, however, now known that the property and performance of functional materials must also rely on hierarchical structures across a broad spectrum of length scales, in particular, from 1 to 100 nm [1,2]. Only properly and precisely defined hierarchical structures could enable the transferring and amplifying molecular functions to macroscopic properties [3,4]. However, classical polymer synthetic methodologies are not sufficient to fulfill the precise control over secondary, tertiary and quaternary structures. It is particularly true when ordered structures have supramolecular lattices with building block sizes much larger than common monomers. In this case, collective secondary interactions with sufficiently strong energy levels become extremely critical to stabilize these structures.

To precisely and simultaneously control structures across multiple length scales is a difficult and challenging task. We often rely on serendipity in the discovery of new materials with novel structures/compositions and exotic properties/functions. A better approach is desired. For the past half century, various modular approaches have been proposed in different research fields. For instance, Corey described long time ago about general methods for the construction of complex molecules [5]. Desiraju proposed a concept of "supramolecular synthon" in crystal engineering [6]. Our group also proposed a "retro-functional analysis" (RFA) as a tentative and preliminary strategy for molecular design in soft matter engineering using artificial domains named "structural and functional synthons" [7–9]. The advantage of this rational and modular approach lies on the precise and reliable construction of the designed molecules from the precursor nanobuilding blocks by using highly efficient and selective chemical transformations.

In our researches for developing hybrid functional materials, molecular nanoparticles (MNPs) play a critically important role. These MNPs are compact and rigid nanobuilding blocks with precisely defined symmetry and surface functionality. They include fullerene (*e.g.*, C_{60}), polyhedral oligomeric silsesquioxane (POSS), polyoxometalate, and folded proteins, just to name a few. Among them, POSS has emerged as an important class of molecular organic-inorganic hybrid materials possessing a nano-sized silicate cage core with organic moieties at each corner [10–20]. In this feature article, we focus on the recent advance in the design and functionalization of POSS molecules via "click" chemistry as modular building blocks for hybrid materials. The general chemical formula for POSS molecules is $(\text{R-SiO}_{1.5})_n$, where n is commonly 6, 8, 10, and 12. The diversity of rigid cores with defined symmetry and peripheral groups distributed in three dimensional (3D) space has offered great impetus in exploiting their interesting properties. Moreover, the small structure of the rigid silica cube in POSS could be useful for clustering a large variety of functional molecules into the compact space. It makes these nanoscale organic-inorganic hybrid materials competitive candidates for applications in a variety of fields ranging from soft electronics to nanomedicine [14–16].

Currently, there are over 3000 scientific reports on POSS-based hybrid materials (data from SCOPUS). Yet, it remains a challenge to precisely and rapidly prepare functional materials on larger scales by design [17,21,22]. Concern has arisen over the low yield and high production cost as a result of the tedious synthesis often encountered in the pursuit of exceptionally high structural complexity required for specific functions and applications [10,21]. Considering the wide-ranging applications of organic-inorganic hybrids, it is necessary to develope a rapid, versatile and highly efficient method for target-oriented, readily adaptable rational design and facile synthesis of commercially competitive hybrid materials [10].

Recent advances in the filed of organic and materials chemistry have offered the opportunity to "click" assemble hybrid materials based on different POSS building blocks. "Click" chemistry, proposed and defined by Sharpless et al. [23], as chemical philosophy in 2001, invokes several nearly perfect "spring-loaded" chemical reactions with high thermodynamic driving forces and serves as a powerful and popular strategy in the quest for rapid and modular synthesis in polymer chemistry and material science [24–30]. Typical "click" reactions include Cu(I)-catalyzed [3 + 2] azide-alkyne cycloaddition (CuAAC), strain-promoted azide-alkyne cycloaddition (SPAAC), Diels–Alder cycloaddition, thiol-X reaction (TEC), and oxime ligation. They are not perfect, but they exhibit several features of an ideal "click" reaction. Notably, it is still challenging to modify all vertices onto POSS surface due to the steric hindrance of the cubic silica. In contrast, by applying the click reactions, the desired products can be obtained in relatively good yields. More interestingly, the combination of multiple "click" reactions provides new opportunities to fabricate multifunctional materials in a simple and elegant way. We will elaborate on these powerful chemical tools with focus on their applications in POSS-related materials. Representative examples will be shown to demonstrate the power of multiple "click" reactions in complexity- and diversity-driven synthesis. It will be self-evident that the click philosophy wholly coincides with the goal of modular manipulation of the desirable hybrid material structures and performances, opening up broad avenues and fast tracks to advanced POSS-based functional materials.

2. “Click” chemistry toolbox

Over the past decade, it has been increasingly recognized that “good” reactions for making POSS-related materials shall meet three main criteria, namely efficiency, versatility, and selectivity. Since POSS molecule is not stable under basic or other harsh conditions, “click” reactions are ideal tools for preparing various POSS-conjugates without compromising the structural and functional integrity of POSS core. So far, most “click” reactions have been applied to conjugate POSS with other motifs or for multi-site functionalization of POSS (Fig. 1). The recent emerging “click” reactions, like tetrazine cycloaddition [31] and genetically encoded SpyTag–SpyCatcher chemistry [32,33], might also be used to prepare POSS-based biohybrids.

The concept of “click” chemistry was first proposed in 2001 and the CuAAC was later shown to be a typical “click” reaction [23,34]. This reaction has allowed scientists to prepare functional POSS-based hybrid materials with an impressive variety, since it offers nearly quantitative yields, a wide range of solvent tolerance, and exceptional stability of the resulting triazole products. Using this reaction, many POSS building blocks have been successfully coupled with a library of macromolecules with diverse chemical compositions and complex architectures, including polystyrene (PS), poly (ethylene oxide) (PEO), diblock copolymer PS-PEO, and cyclic polymers, etc. The only drawback may be the small amount of copper residues which may be toxic for bio-related applications [17]. It should also be noted that the coupling efficiency of CuAAC might be compromised in the presence of multiple –COOH/-OH/-NH_2 groups as in bio-hybrid preparations.

As an alternative to CuAAC, SPAAC between cyclooctynes and azides has emerged as a bio-orthogonal, metal-free, and highly efficient “click” chemistry [35,36]. The introduction of ring strain strongly decreases the activation energy for the cycloaddition. Even in the absence of Cu(I), cyclooctyne could rapidly react with azide in high yields at ambient conditions. Notably, 4-dibenzocyclooctyne (DIBO) is the most widely used cyclooctyne motif for POSS-polymer conjugation. Although it generates a mixture of regioisomeric products, it is usually not a major issue in the current materials design [37]. It can also be addressed by using symmetric cyclooctynes such as BCN (bicycle[6.1.0]nonyne) [38]. In addition, the distinctly different chemical reactivity between cyclooctyne and terminal alkyne in the absence of metal catalyst could facilitate a selective functionalization of POSS cage, allowing the further development of multifunctional POSS-based materials [39,40]. Note that although SPAAC was initially designed for bioconjugation, its real applications in synthetic POSS-bioconjugates are still scarce currently [17].

The century-old radical-mediated addition reaction of a thiol across an ene has gained renewed attention as an emerging “click” reaction [41,42]. It proceeds via a radical mechanism, either photo-/thermally-induced, to give an anti-Markovnikov-type thioether product [43–49]. The “click” feature of TEC reaction is recognized since it is highly efficient and orthogonal to a wide range of functional groups and the reaction is compatible with moisture and

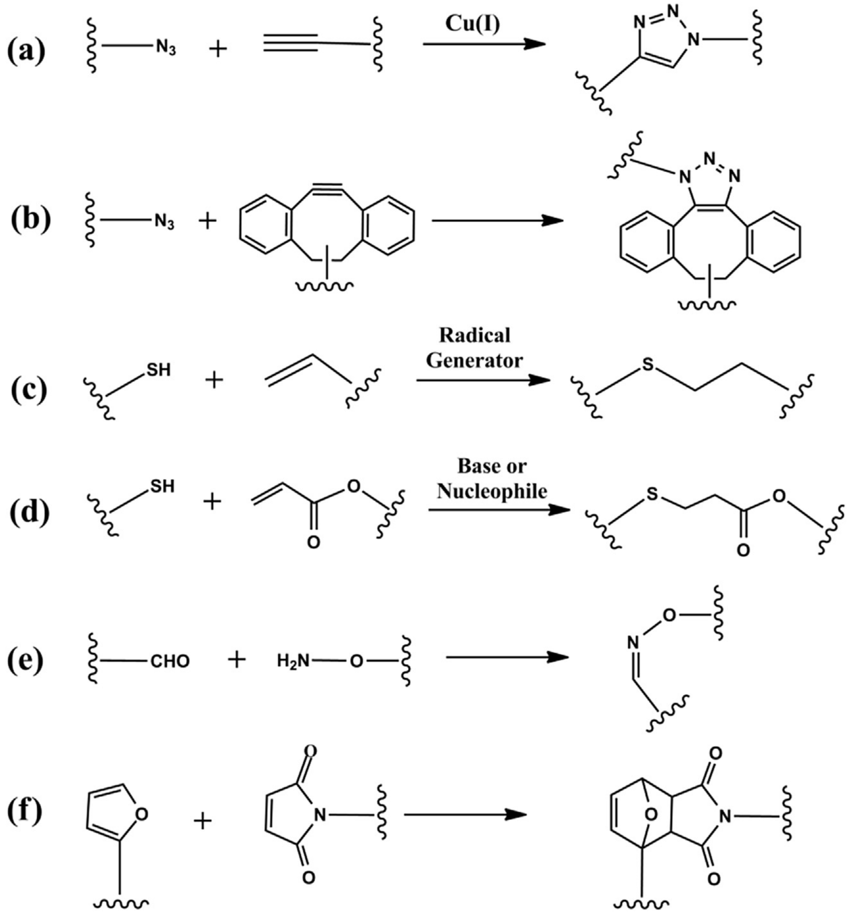


Fig. 1. Overview of “click” reactions for preparing POSS-based hybrid materials: (a) CuAAC, (b) SPAAC, (c) TEC, (d) thiol-Michael addition, (e) oxime ligation, and (f) Diels–Alder reaction.

oxygen. More importantly, it forms a thioether linkage stable in a wide range of chemical environments. It was first used as a facile and convenient way to prepare octaPOSS-based glycoclusters [50]. Shortly thereafter, several examples for the peripheral multi-site modification of VPOSS (vinyl group-functionalized POSS) or VPOSS conjugated precursors (i.e. VPOSS-polymer, VPOSS-nanobuilding block) with a myriad of different thiol functionalities (including hydrophilic groups [39,51–58], hydrophobic groups [54,59], fluorophilic functionalities [60–62], and bioactive moieties [56]). Recently, it was used as a simple approach to Janus POSS building blocks, including a complete series of monoadduct (C_{3v}), diadduct regio-isomers (C_{2v}(*ortho*-), C_{2v} (*meta*-), and D_{3d} (*para*-)), and triadduct regio-isomers (C_s (*oom*-), C_s (*omp*-), and C_{3v} (*mmm*-)) [63–65].

Thiol-Michael reaction describes the base/nucleophile-mediated "click" addition of a thiol group across activated double bonds [44,66]. Besides its high coupling efficiency, it also circumvents the possibility of radical side-reactions in TEC, which is particularly suitable for POSS functionalization with bulky ligands or UV-attenuating functional groups with minimum side products [67,68].

The oxime ligation describes the efficient condensation reaction between an aminoxy group and an aldehyde or ketone to generate an oxime linkage and has attracted increasing attentions as another "click" reaction under physiological conditions [69,70]. This methodology is chemoselective and compatible with most functional groups found in common biomolecules/macromolecules [71]. Notably, considering its orthogonal nature to other "click" reactions, oxime ligation was ideal to achieve one-pot or sequential concise synthesis of POSS-based functional materials [72,73].

Diels-Alder reaction was invented by Otto Diels and Kurt Alder (Nobel laureates in 1950) and has become one of the most established reactions in organic chemistry. It involves a straightforward [4 + 2] cycloaddition reaction between an electron-rich diene and an electron-poor dienophile to form a stable cyclohexene product [74]. Diels-Alder reactions are thermally reversible (retro-Diels-Alder). The decomposition reaction can be well controlled by temperature. Such an interesting feature could be utilized to develop thermally mendable, self-healing, cross-linked POSS networks [75].

Expanding the scope of POSS bioconjugates to proteins, nucleic acids, membrances, or even cells would require more "click" reactions compatible with biological environments [4]. Tetrazine ligation, a unique inverse Diels–Alder reaction between tetrazines and strained dienophiles, has been widely used in live cell imaging and animal labeling and may be useful for preparing POSS-based fluorogenic nanoparticle probes in this regard [31]. The genetically encoded SpyTag–SpyCatcher chemistry describes the autocatalytic "bioorthogonal" ligation between peptide tag (SpyTag) and its protein partner (SpyCatcher) to rapidly form isopeptide bond [32,33]. This methodology serves as the bridge between synthetic materials and proteins.

3. "Clickable" POSS building blocks

To apply "click" reactions, the POSS cages must first be made "clickable", which is usually achieved either by direct cohydrolysis of functional silanes with "click" functionalities, or post-condensation substitution to attach "clickable" group(s). Fig. 2 shows a summary of "clickable" POSS building blocks that have been successfully synthesized and used in literature. Specifically, "clickable" groups refer to alkynes, cyclooctynes, alkenes, azides, thiols, amines, etc. The increasing structural and functional complexity of final materials also necessitates the preparation of POSS with more than one types of "click" functionalities, which will be elaborated in the following subsections.

3.1. POSS with single kind of "click" functionality

3.1.1. Homofunctional POSS building blocks

Homofunctional POSS contains single type "click" functionality at all corners (Fig. 2 and Table 1). They can be prepared either by full hydrolysis of "clickable" trimethoxysilane monomers, or via chemical transformation from a homofunctional POSS precursor. The multiple reactive sites on POSS present the opportunity to fabricate multifunctional materials with one "click" reaction. Azido-functionalized POSS compounds (N_3POSS) are the most popular precursors for either CuAAC or SPAAC to modularly introduce alkynyl- or cyclooctyne-functionalized moieties. The N_3POSS can be easily synthesized via nucleophilic azidation of halogens with NaN_3 [76,77] or diazo-transfer reaction of amines with nonafluorobutanesulfonyl azide [78]. In the former, the cage scrambling during azidation would yield a mixture of T_8, T_{10}, and T_{12} POSS cages, which can be isolated in satisfactory yields [76,77]. So far, azide-functionalized T_8-, T_{10}-, and T_{12}-POSS building blocks have been reported and employed as useful scaffolds for soft materials including supramolecular dendrimers [79], shape amphiphiles [77], multivalent bioconjugates [78,80,81], and star-shaped hybrid polymers [82–84]. Besides N_3POSS, many kinds of multiple alkyne-functionalized POSS (alkyne-POSS) and cyclooctyne-functionalized POSS (cyclooctyne-POSS) precursors have been designed and synthesized via simple multi-site coupling reaction like esterification or amidation [85–89].

Alkene-containing POSS compounds are advantageous for making porous organic-inorganic hybrids [109,110,116,137] and bioactive materials [50,138]. Typical ones include commercially available octavinyl POSS (VPOSS) [50] and octaacryloxyl-functionalized POSS (ACPOSS) [68,117], allowing facile simultaneously, multi-site functionalization by using TEC or thiol-Michael reaction, respectively. Nevertheless, both building blocks are generally a mixture of fully condensed products, from which well-defined T_8/T_{10}/T_{12} products may be purified by re-crystallization or column chromatography [68]. Their surface chemistry can then be easily and efficiently tuned from hydrophilic [52,111,112,139] and hydrophobic groups [113], to fluorophilic functionalities [62], and even to bio-moieties [138]. Alternatively, octamercaptopropyl POSS (HSPOSS) was also synthesized via the hydrolysis of (3-mercaptopropyl) trimethoxysilane monomer [117,122–124,140–142]. This building block has been widely used to react with multiacrylate-based materials to generate several highly cross-linking systems, such as hybrid inorganic/organic networks [117,122], nanoimprint lithography photoresists [123], and responsive hybrid vesicles [124].

Oxime ligation also serves as a powerful and metal-free tool for attaching bioactive agents onto POSS. Both octaaminopropyl POSS (NH_2OPOSS) [71] and octaaldehyde-bearing POSS (CHOPOSS) [118] have been designed and prepared as multifunctional precursors for oxime ligation. The former was synthesized by acylation of commercially available octaaminopropyl POSS (T_8 NH_2POSS) with butoxycarbonyl (Boc) aminooxy acetic acid and subsequent deprotection [71], while the latter was prepared by hydrosilylation of T_8 VPOSS with protected aldehyde silanes [118]. It was found that the efficiency of oxime ligation highly depended on the steric hindrance and electrostatic repulsive interaction of used biomolecular ligands like peptides and proteins [71]. Finally, octafuran-bearing POSS has also been prepared by reacting T_8 epoxy-modified POSS cage with furfurylamine as a promising percursor for thermally reversible DA functionalization [75].

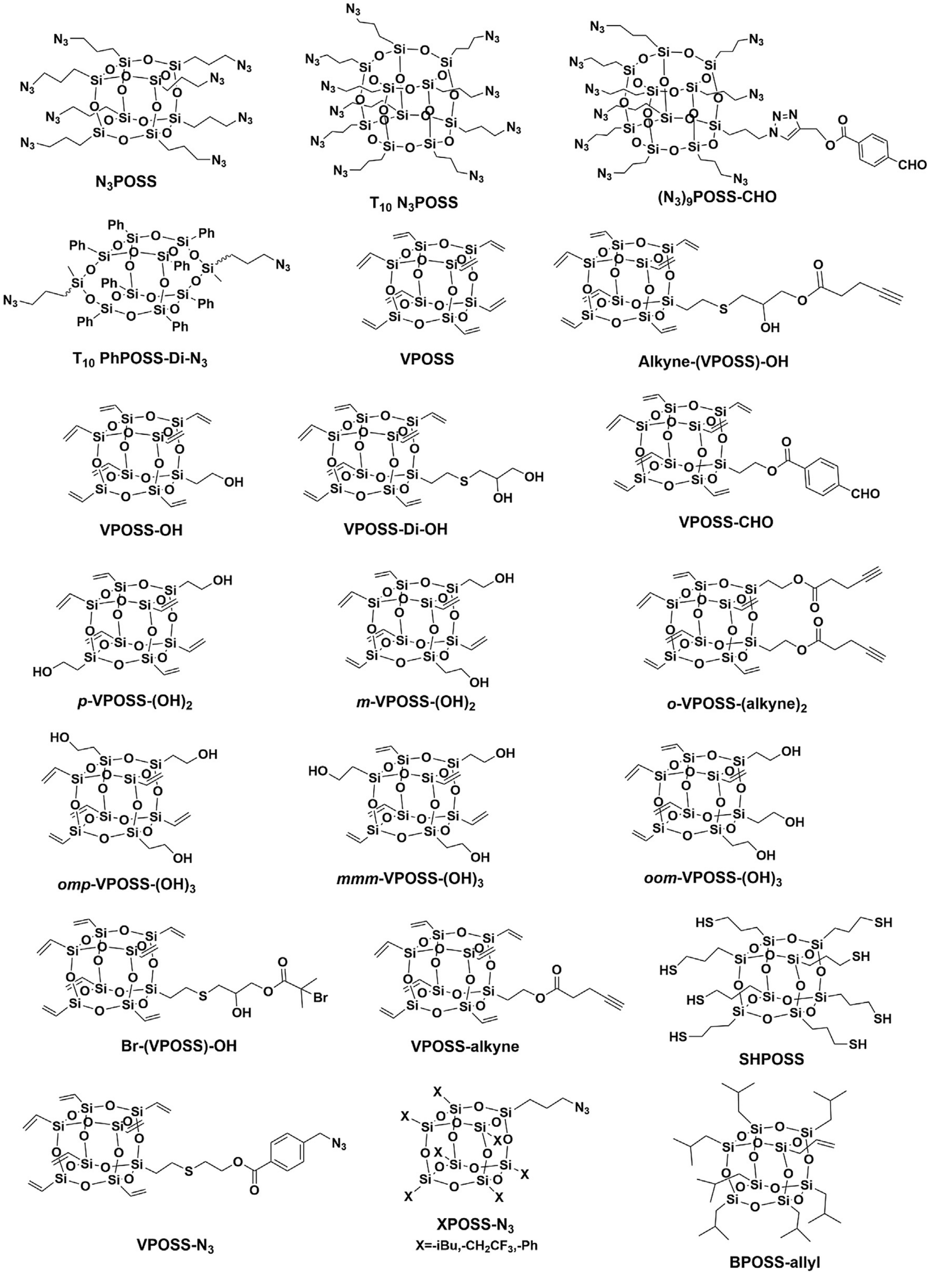
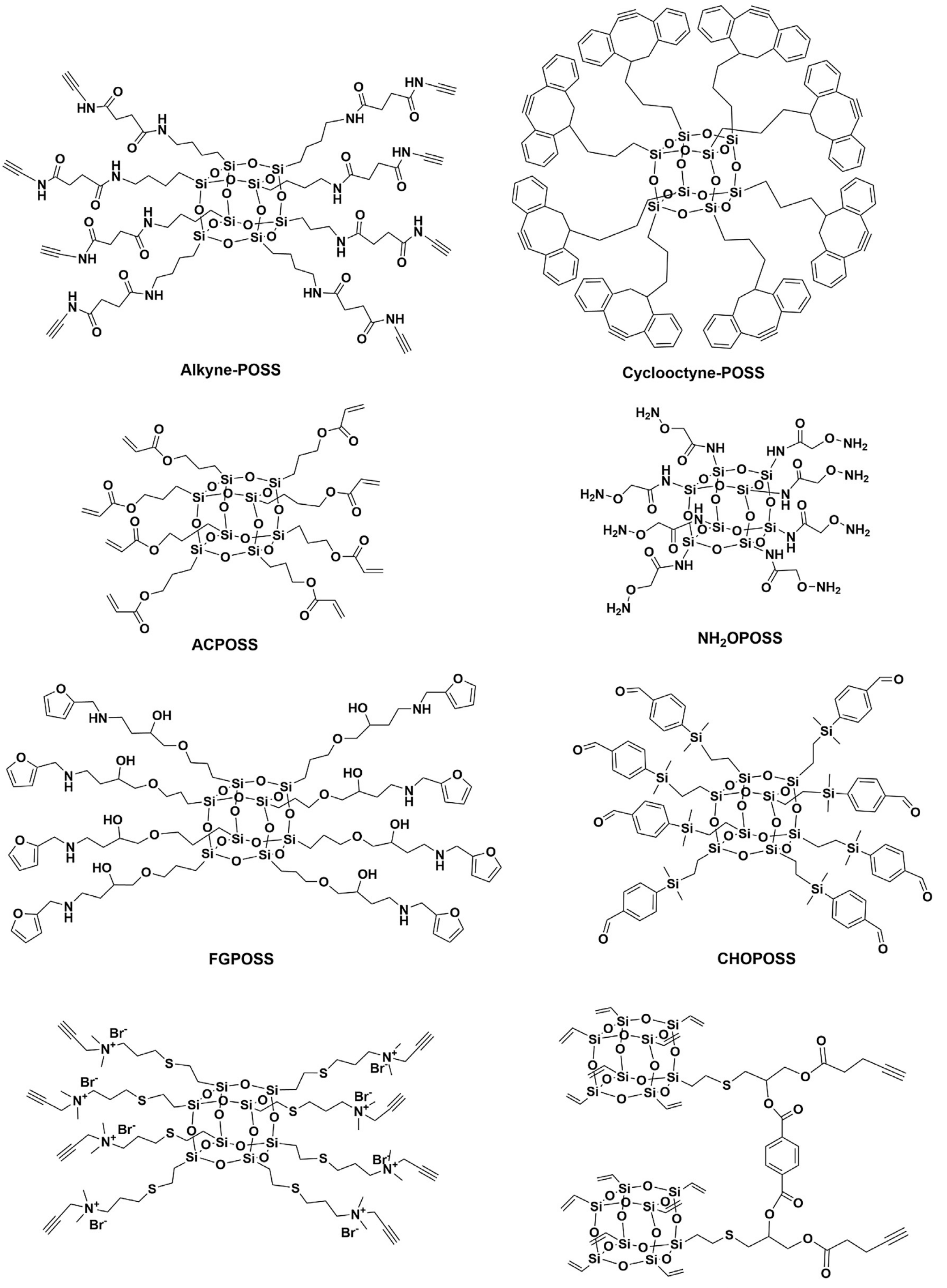


Fig. 2. General scheme for "clickable" POSS building blocks.

3.1.2. Heterofunctional POSS building blocks

Heterofunctional POSS derivatives possessing two kinds of addressable chemical groups (one of them allows the "click" conjugation) are usually generated either by corner-capping reactions of incompletely condensed POSSs, or via selective side group modification of an intact POSS cage [14]. The resulting building blocks are ideal start materials for making heterogenous hybrids with tuanble macroscopic properties and self-assembly



Alkyne-POSS

Cyclooctyne-POSS

ACPOSS

NH_2OPOSS

FGPOSS

CHOPOSS

Alkyne-POSS

$(VPOSS\text{-}alkyne)_2$

Fig. 2. (*continued*).

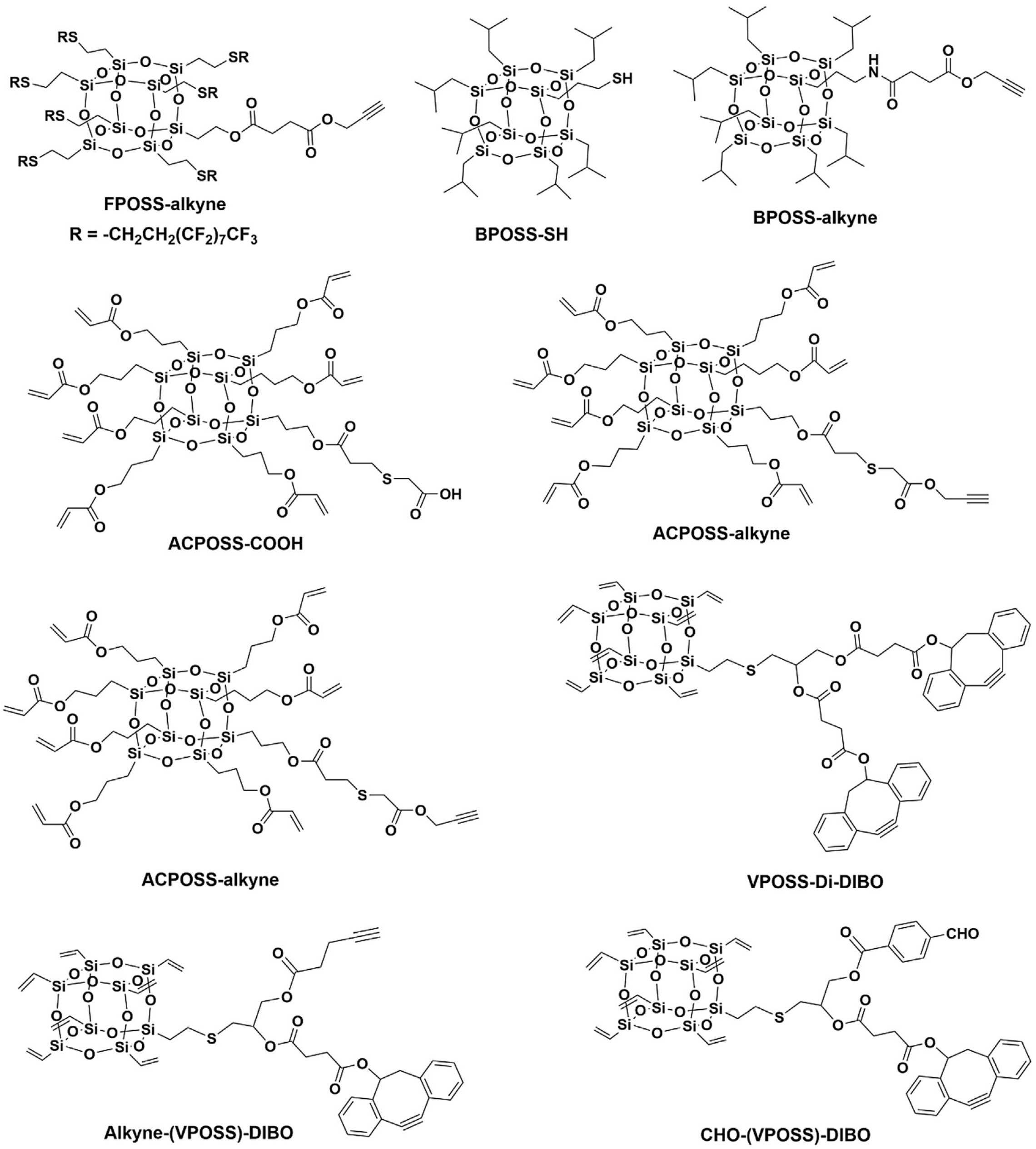


Fig. 2. (*continued*).

behaviors. In the past several years, the utilization of stoichiometry-controlled "click" functionalization of homofunctional POSS compounds has been demonstrated to be an efficient way toward multifunctional building blocks [63,81]. It greatly improves the functional group tolerance during functionalization, and the remaining "clickable" groups on POSS surface could be subjected to further derivatization. Chiara's group pioneered this study by using ligand-accelerated CuAAC functionalization of T_8 N_3POSS at the first step to obtain heterofunctional POSSs bearing one adduct with seven azido groups for subsequent hepta-CuAAC functionalization to prepare fluorescent multivalent probes for targeted cell-imaging [81]. Our group has also demonstrated TEC as a facile, general and convenient approach towards a series of well-defined mono-functional VPOSS building blocks with C_{3v} symmetry [63].

For heterofunctional T_8 POSS cages, the "clickable" functionality can be either on the pendant positions or on the seven periphery groups of a POSS cage. A majority of established "clickable" POSSs belong to the former category. The most important building block in the latter category is PSS-(3-hydroxyethyl)-heptavinyl substituted (VPOSS-OH), invented by Feher et al. [143]. The synthetic procedure involves the addition of triflic acid across the double bonds in T_8 VPOSS followed by hydrolysis in wet acetone. The rich chemistry of hydroxyl and vinyl groups allows efficient and orthogonal functionalization to give various interesting functional materials. For example, the hydroxyl group can be used to directly initiate the ring-opening polymerization [56,60], or converted to other functional groups via esterification; the vinyls are readily modified by Thiol-X reactions. Thus, VPOSS-OH is one of the key building blocks that can be converted into many POSS derivatives containing two or more kinds of "clickable" groups [54]. Notably, a similar building block can also be prepared by TEC mono-

Table 1
Summary of “clickable” POSS building blocks allowing for various “click” conjugations.

Building Block	“Click” Reaction	Functional Molecule	Product	Year	Ref.
T_{10} N_3POSS	CuAAC	Alkynyl Crown ether	Dendrimer	2011	[79]
T_{10} N_3POSS	CuAAC	Alkyne-CHO	Shape Amphiphile	2014	[77]
BPOSS-N_3	CuAAC	Dibenzylammonium alkyne	Dendrimer	2011	[79]
$(N_3)_9$POSS-CHO	Oxime Ligation	NH_2O-PS	Shape Amphiphile	2014	[77]
N_3POSS	CuAAC	Alkyne-PEO	Polymer	2013	[82,83]
N_3POSS	CuAAC	Alkyne-PLLA	Polymer	2013	[83]
N_3POSS	CuAAC	Propargyl 2-Bromoisobutyrate	Macro-initiator	2009	[84]
N_3POSS	CuAAC	Alkyne-RDG8 peptide	Bioconjugation	2010	[90]
N_3POSS	CuAAC	Alkyne-BDP dye	Dye	2011	[91]
N_3POSS	CuAAC	P-pa	Nanocomposite	2010	[92]
N_3POSS	CuAAC	Alkyne-PEO-alkyne	Hydrogel	2009	[93,94]
POSS-N_3	CuAAC	1,1,1-tris [4-(2-propynyloxy)- phenyl]-ethane, PEG-b-PMMA-alkyne	Star Polymer	2010	[95]
POSS-N_3	CuAAC	Alkyne-PS50-polyDVB	Star Polymer	2010	[96]
POSS-N_3	CuAAC	Propargyl 2-chloropropionate	Polymer	2012	[97]
POSS-N_3	CuAAC	PBiB, alkyne-PMMA	Polymer	2010	[98]
POSS-N_3	CuAAC	Alkyne-PBLG	Nanoparticle	2011	[99]
POSS-N_3	CuAAC	Alkyne-PNBMA	Micelle	2015	[100]
POSS-N_3	CuAAC	PPLG	Micelle	2012	[101]
POSS-N_3	CuAAC	Alkyne-PS	Micelle	2012	[102]
POSS-N_3	CuAAC	P (MMA-co-HEMA)-alkyne	Nanocomposite	2013	[103]
POSS-N_3	CuAAC	Bis(propargyl)benzene	Polymer	2010	[104]
POSS-N_3	CuAAC	Alkyne-ZnTPP	Micelle	2015	[105]
POSS-N_3	CuAAC	Alkyne-PNIPAm	Star Polymer	2012	[106]
POSS-N_3	CuAAC	Alkyne-PBLG	Star Polymer	2010	[107]
POSS-DIBO	SPAAC	N_3-fluorescein, N_3-Lactose, N_3-PEG	Nanoparticle	2015	[89]
VPOSS	TEC	SH-PEG, TGA	Porous Material	2011	[108,109]
VPOSS	TEC	HDT	Porous Film	2014	[110]
VPOSS	TEC	SH-glycocluster	Glycocluster	2004	[50]
VPOSS	TEC	MPS	Nanoparticle	2013	[111]
VPOSS	TEC	Cysteamine Hydrochloride	Polymer	2014	[112]
VPOSS	TEC	1-dodecanethiol	Antioxidant	2013	[113]
VPOSS	TEC	PEG-SH, Glycoside-SH, Peptide-SH	Scaffold	2012	[114]
ACPOSS	TEC	5A, P8A	Fiber	2016	[115]
MAPOSS	TEC	HDT, TPTM, PTM	Monolith	2015	[116]
MAPOSS	TEC	POSS-SH	Network	2013	[117]
VPOSS-OH	TEC	2-mercaptoacetic acid	Janus particle	2011	[58]
FPOSS-alkyne	CuAAC	N_3-PS	Giant Surfactant	2013	[52]
CHOPOSS	Oxime Ligation	4-bromo-3,5-bis [(dimethylamino)methyl] aniline	Dendrimer	2001	[118]
VPOSS-alkyne	CuAAC, TEC	mPS-N_3, 1-thioglycerol	Shape Amphiphile	2013	[119]
VPOSS-alkyne	CuAAC, TEC	CPS-N_3, 1-thioglycerol	Giant Surfactant	2014	[120]
VPOSS-alkyne	CuAAC, TEC	BPOSS-N_3, 1-thioglycerol	Giant tetrahedra	2015	[121]
SHPOSS	TEC	Epoxy Acrylate	Hybrid Curing Network	2013	[122]
SHPOSS	TEC	BMA, TMPT	Hybrid Curing Polymer	2011	[123]
SHPOSS	TEC	A-PEA	Vesicle	2011	[124]
T_{10} POSS-DiN_3	CuAAC	α,w-dialkynyl-terminated oligoethylenes	Copolymer	2013	[125]
Alkyne-POSS	CuAAC	N_3-PMMA	Polymer Conjugate	2011	[85]
Alkyne-POSS	CuAAC	N_3-PS, N_3-PS-N_3, Glu-PS-N_3	Polymer Conjugate	2010	[126]
Alkyne-POSS	CuAAC	PS-(CH_2N_3)m	Polymer Conjugate	2013	[127]
Alkyne-POSS	CuAAC	N_3-PtBA-N_3	Polymer Conjugate	2011	[128]
Alkyne-POSS	CuAAC	SEBS-CH_2N_3	Polymer Conjugate	2013	[129]
POSS-SH	TEC	Alkyne-PBLG	Vesicle	2011	[130]
POSS-SH	TEC	TMPTA	Microcapsule	2013	[131]
POSS-OA-SH	TEC	ACO	Network	2011	[132]
F_2-POSS-SH_6	TEC	HDDA, A-BPE-10	Coating	2012	[133]
OBVN_3-POSS	CuAAC	9-(prop-2-ynyl)-9H-purin-6-amine	Network	2012	[134]
DIBO-VPOSS-CHO	SPAAC, Oxime Ligation, TEC	PS-N_3, NH_2O-PS, 2-mercapoethanol	Giant Surfactant	2016	[135]
FGPOSS	DA	MPBMI	Nanocomposite	2013	[75]
VPOSS-alkyne	CuAAC, TEC	N_3-PS, N_3-PEO, 2-mercaptoacetic acid, 1-thioglycerol, 2-mercaptoethanol, 1- hexanethiol	Giant Surfactant	2012	[54]
VPOSS-di-OH	TEC	2-mercapoethanol	Giant Surfactant	2012	[57]
ACPOSS-alkyne	CuAAC, Thiol-Michael	N_3-PS, 1H,1H,2H,2H-perfluoro-1-decanethiol	Giant Surfactant	2014	[68]
VPOSS-di-DIBO	SPAAC, TEC	N_3-PS, 1H,1H,2H,2H-perfluoro-1-decanethiol	Giant Surfactant	2015	[40]
yne-$(VPOSS)_2$-yne	CuAAC, TEC	N_3-PS, 2-mercaptoacetic acid	Giant Surfactant	2013	[55]
Alkyne-(VPOSS)-DIBO	CuAAC, SPAAC, TEC	N_3-PCL, N_3-PS, 2-mercapoethanol	Giant Surfactant	2013	[39]
CHO-VPOSS-DIBO	Oxime Ligation, SPAAC, TEC	NH_2O-PS, N_3-PS, 2-mercapoethanol	Giant Surfactant	2013	[72]
CHO-VPOSS-DIBO	Oxime Ligation, SPAAC, TEC	N_3-PS, “click” adaptor, 2-mercaptoacetic acid, 1-thioglycerol	Giant Surfactant	2016	[135] [136],

functionalization of VPOSS with 2-mercaptoethanol [63]. We have further designed a “clickable” POSS compounds with two hydroxyl groups at one pendent position and seven vinyl groups, VPOSS-Di-OH, which is a monoadduct from the TEC monoadduct of 1-thioglycerol with VPOSS [57,63]. Interestingly, the distinct reactivity of two hydroxyls enables the selective esterification of the primary hydroxyl to give a series of multifunctional VPOSS derivatives. Similarly, another heterofunctional “clickable” POSS containing on carboxylic acid and seven activated enes, ACPOSS-COOH, has been achieved based on the mono-functionalization of T_8 ACPOSS [68]. It has been used to design and synthesize giant surfactants with bulky ligands at the POSS periphery [68].

The regio-selective synthesis of precisely-defined di-and tri-POSS adducts presents a considerable challenge, especially on synthetically useful scales [63,65,81,144]. It has been found that TEC modification of VPOSS with bulky thiol ligands lead to improved selectivity for the *para*-diadduct due to steric hindrance. The electrospray ionization mass spectrometry (ESI) coupled with travelling wave ion mobility (TWIM) separation was employed to isolate and characterize the crude di-adduct products [63]. A similar concept was employed by Chiara's group to successfully prepare the di-functional POSS nanocubes via the symmetry-controlled multiple CuAAC “click” functionalization of T_8 N_3POSS with a conformationally constrained di-alkyne with an appropriate spatial orientation of the triple bonds (Fig. 3). Note that the majority of crude product is “on-edge” bis-triazolyl POSS, while both of the “face-diagonal” and “cube-diagonal” regio-isomers can not be observed by HPLC-ESI analysis of the crude product, probably due to the steric hindrance [144]. This group continued to use the similar strategy to successfully synthesize the Janus POSS nanocube with two chemically distinct opposed faces for future hybrid materials development [144]. Note that this is the first time to prepare Janus POSS nanocube via direct multiple functionalization of an existing POSS, while the pervious strategy usually involves the cross-coupling of a“half-cube” cyclic sodium siloxanolate with another half-cube cyclicfluorosiloxane [145].

In addition, Zhang and co-workers successfully isolated and characterized a complete series of di- and tri-VPOSS adducts in gram quantities following the modified Feher's method (Fig. 4) [64]. The successful isolation by flash column chromatography may be due to their distinct dipole moments and polarity as well as the cooperative multidentate effect of hydroxyls. The resulting “clickable” Janus POSS building blocks enable the synthesis of mixed [2:6] hetero-arm star polymers with precisely arranged polymeric arms in space [146] and the elucidation of the effect of regio-configuration of the assembly of giant surfactant regio-isomers [147].

Another important family of POSS cages with single “click” functionality, which involves a hydrophobic/fluorinated POSS cage and a “clickable” group (i.e. azido, alkyne, thiol, vinyl, *etc.*) on the pendant position, can be prepared either via stoichiometrically controlled single-corner ligation or by the corner capping of incompletely condensed POSS with silanes bearing “clickable” groups. For instance, azido-tethered heptaX-substituted POSS (XPOSS-N_3) (where X is isobutyl, phenyl, fluoropropyl …) was commonly synthesized by azidation reaction of XPOSS-Cl/-Br precursors with high yields, which could further (1) conjugate with different alkyne-terminated polymers including PEO [93–95,148], poly (*tert*-butyl acrylate) (P*t*BA) [96], poly (N-isopropylacrylamide) (PNIPAAm) [97], poly (γ-benzyl-*l*-glutamate) (PBLG) [99], poly (methyl methacrylate) (PMMA) [98], PS [96,98], and amphiphilic co-polymers [100]; (2) attach onto polymeric backbones as the nano-sized side chain moieties [101–104,149]; (3) couple with other functional nanomaterials using CuAAC reaction [96,104,105,150–152]. Additionally, diazido-functional T_{10} POSS (3,13-azidopropyloctaphenyl double-deck-shaped T_{10} POSS), was designed and synthesized by Kawakami's group (Fig. 5) [76]. They employed an incompletely condensed silsesquioxane [153] as the precursor to react with (3-chloropropyl)-methyldichlorosilane to get the double-decker precursor, followed by azidation with excess NaN_3 in DMF/THF mixed solvent (v/v = 7/2) at 60 °C (Fig. 5). Note that it contains two “clickable” sites, which offers opportunities for making more complex nanohybrids [125]. Correspondingly, XPOSS cages with alkyne functionality as the pendant group (XPOSS-

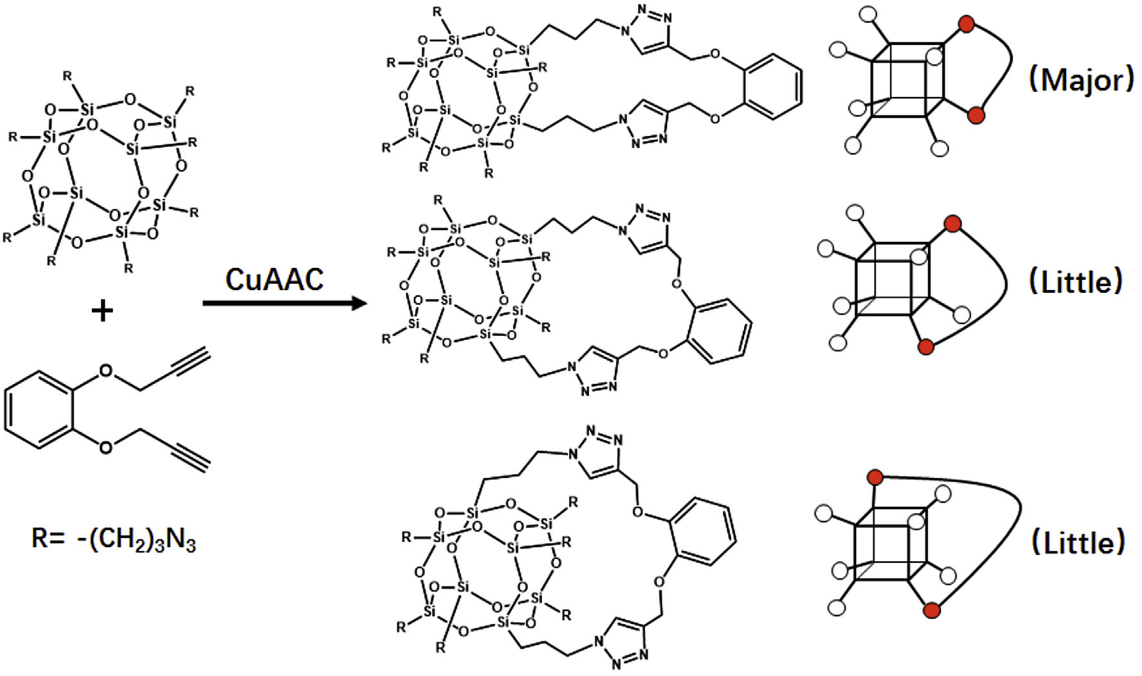


Fig. 3. Synthesis of di-functional POSS nanocubes via the symmetry-controlled multiple CuAAC “click” functionalization of T_8 N_3POSS [144].

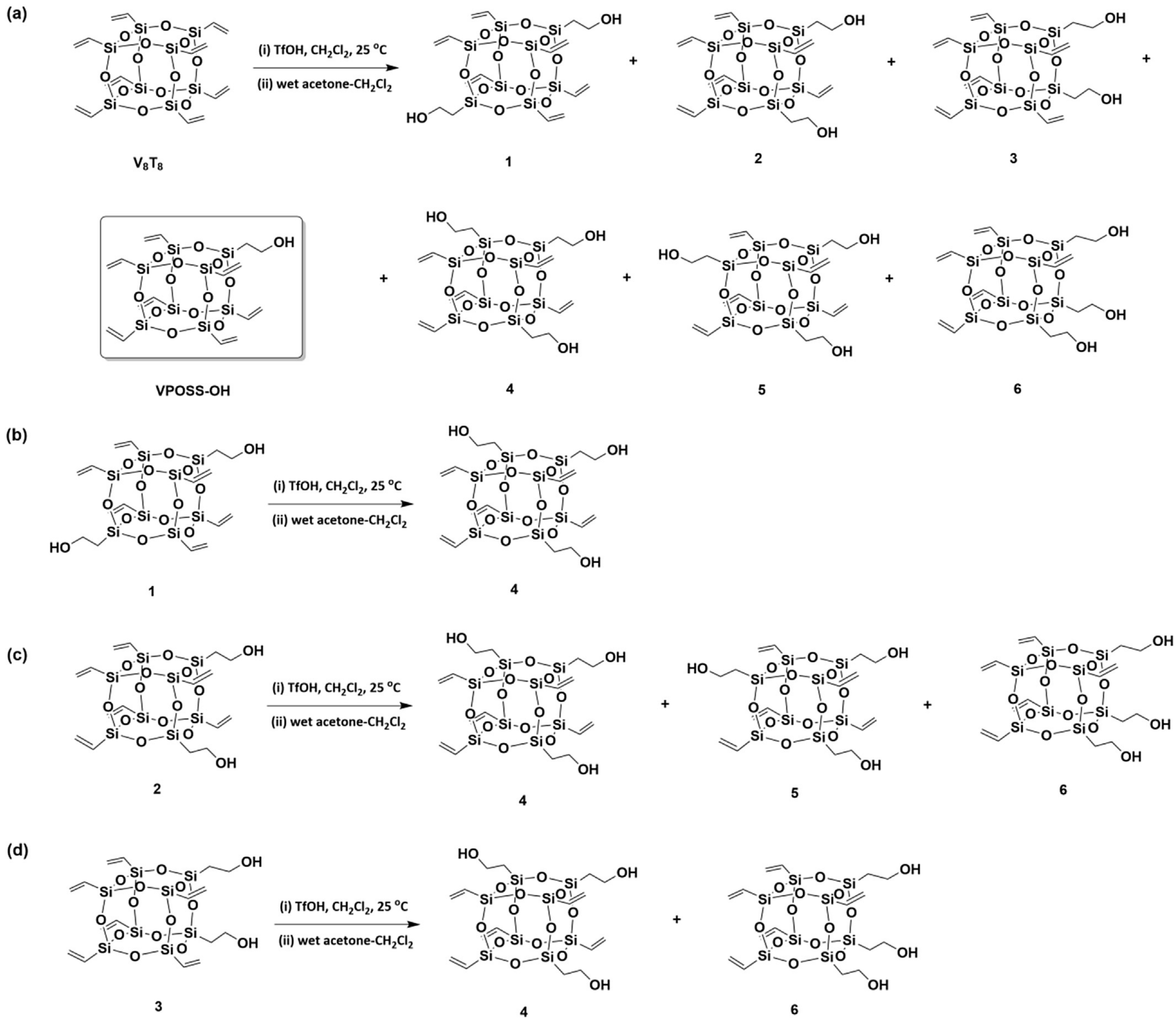


Fig. 4. (a) Synthesis of mono-, di-, and triadducts. (b-d) Synthesis of triadducts from individual diadducts. (TfOH=trifluoromethanesulfonic acid) [64].

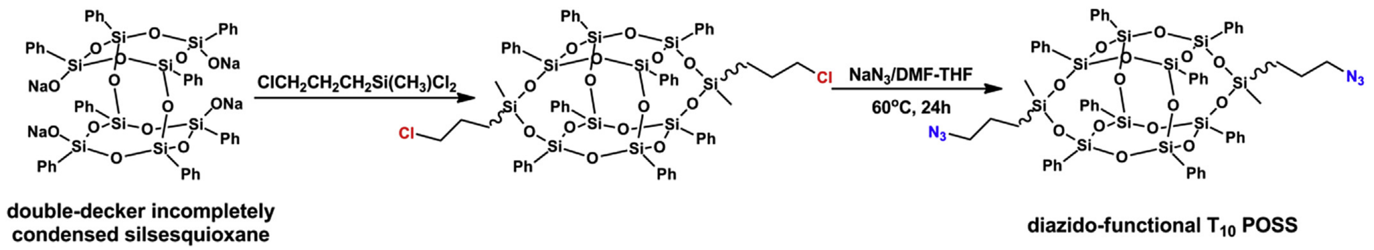


Fig. 5. Synthesis of diazido-functional T_{10} POSS [76].

alkyne) also serve as another family of building blocks to construct funtional hybrids via CuAAC "click" conjugation reaction, and the common way towards XPOSS-alkyne is to employ kinds of POSS precursors (i.e. XPOSS-OH/-NH_2/-COOH) to couple with small molecular alkynes via different simple conjugation reactions [61,126–129,154].

Mercaptopropyl isobutyl POSS (BPOSS-SH) is a commercial available building block with single "click" thiol functionality [130,155–158]. It has been widely used as a crystalline motif to conjugate with other vinyl-containing molecular objects via thiol-X "click" reactions (i.e. TEC [157], thiol-Michael [158], thiol-yne [130], and thiol-epoxy reaction [156]). Recently, Jiang's group has developed a new class of thiol-contained POSS derivatives mixture (X-POSS-SH, the numbers of X and thiol functionalities are not precisely controlled) via the co-hydrolysis of 3-mercaptopropyl trimethoxysilane and other kinds of functional trimethoxysilane [131–133,159]. The X denotes a wide range of functionalities including hydrophilic [131,159], hydrophobic [132], and fluorophilic moieties [133], based on the selection of functional trimethoxysilane (X-Si(OCH_3)$_3$). Allyl isobutyl POSS (BPOSS-allyl) is also commercially available. Due to high reactivity of allyl group with thiols, BPOSS-allyl can be further transformed into various functional POSS derivatives bearing hydroxyl, carboxyl, ester and trialkoxysilane groups in high yields [127,160].

3.2. POSS cages with two "click" functionalities

POSS building blocks with two or more types of "click" groups allow the use of several orthogonal click reactions. The synthesis could proceed in sequential or one-pot fashion towards multi-functional hybrid materials. It also allows the iterative fractal synthesis [22]. VPOSS-alkyne, obtained by esterification of VPOSS-OH with 4-pentynoic acid, represents the first POSS with two "click" functionalities (Fig. 6) [54]. The pendant alkyne could conjugate with moieties of various composition (i.e. polymer/block polymer/nanopaticle) and topology (i.e. linear, cyclic, and branched) [54,119–121,161] via the first CuAAC reaction, while vinyl groups allow the installation of different surface functionalities via the second TEC reaction.

The versatility of VPOSS-alkyne in constructing POSS-based giant molecules further inspires us to develop other kinds of POSS derivatives with two "clickable" sites, such as VPOSS-CHO [72]. Besides VPOSS-OH, both ACPOSS-COOH [68] and VPOSS-Di-OH [57] have also been used as starting materials for POSS derivatives with two "clickable" groups, such as ACPOSS-alkyne [68] and ACPOSS-N_3 [40]. The latter possesses two hydroxyl groups with different reactivity and offers even more control opportunities for fine tuning of the "clicking" position (Fig. 7). For instance, full esterification of both hydroxyls enables the synthesis of homo-bifuncitonal "clickable" POSS compounds including VPOSS-Di-DIBO and VPOSS-Di-alkyne, useful for making giant lipids with symmetric tails or with macrocyclic tail [40]. Selective esterification of the primary hydroxyl group allows the synthesis of hetero-bifuncitonal "clickable" intermediates such as alkyne-(VPOSS)-OH [55] and CHO-(VPOSS)-OH [72] at the first step and multi-"clickable" POSS derivatives including (VPOSS-alkyne)$_2$ (POSS precursor for giant gemini surfactants) [55], alkyne-(VPOSS)-DIBO [39], and CHO-(VPOSS)-DIBO [72] (POSS precursors for multi-headed/-tailed giant surfactants) at the second step. A general approach towards POSS with double "clickable" groups relies on direct symmetry breaking of the T_8 or T_{10} POSS cages using the functional ligands [63,77]. We have employed TEC mono-functionalization of T_8 VPOSS with thiol-functional azido ligand (SH-N_3) to prepare T_8 VPOSS-N_3 [63]. The T_{10} N_3POSS-CHO can also be synthesized in a similar way, enabling the construction of shape amphiphiles via sequentially performed oxime ligation and CuAAC reactions [77].

3.3. POSS cages with three "click" functionalities

To further broaden the scope of POSS hybrid materials, POSS precursors with triple or even more types of "click" functionalities are highly desirable. So far, it usually relies on two-step consecutive esterification reactions of VPOSS-Di-OH to prepare such POSS derivatives, leading to versatile building blocks like alkyne-(VPOSS)-DIBO [39], and CHO-(VPOSS)-DIBO [72]. Starting from alkyne-(VPOSS)-DIBO, we have demonstrated a general sequential triple

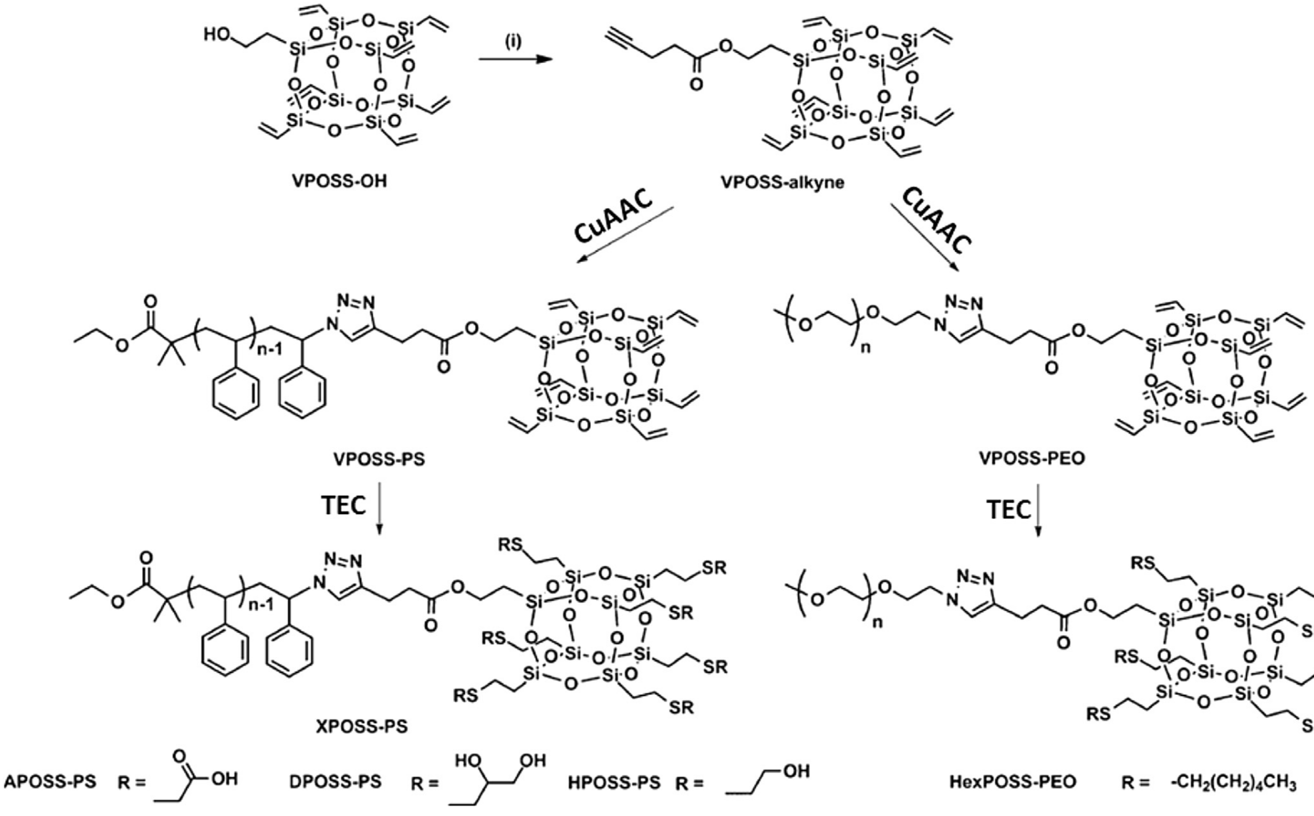


Fig. 6. Sequential "click" synthesis of giant surfactants starting from VPOSS-alkyne precursor [54].

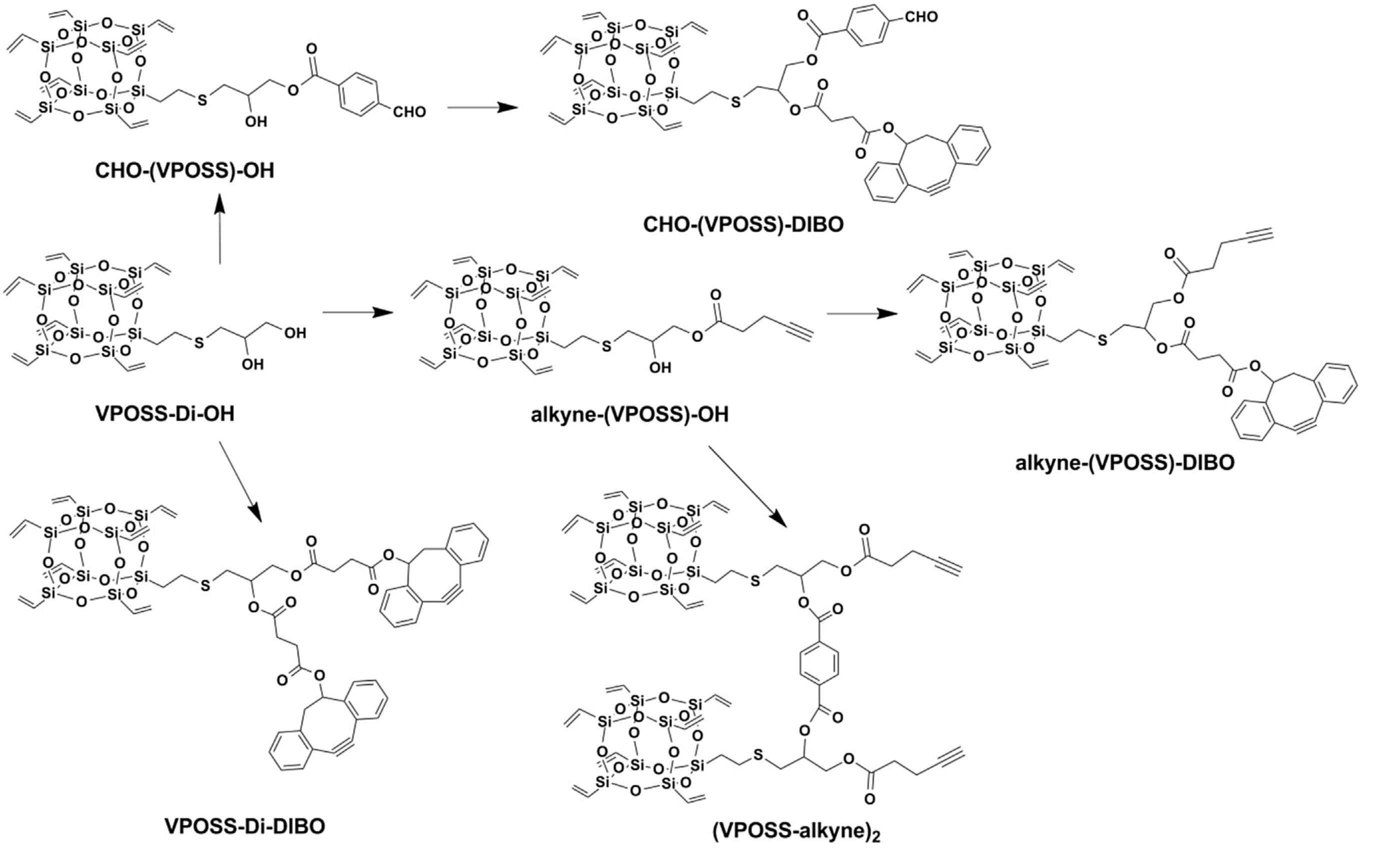


Fig. 7. Synthesis of series of “clickable” POSS building blocks starting from VPOSS-Di-OH [39,40,55,57,63,72,73].

“click” methodology using consecutive SPAAC (with DIBO), CuAAC (with terminal alkyne), and TEC (with vinyl) reactions for the preparation of POSS-based multi-headed/multi-tailed giant surfactants [39]. Although those three reactions are not fully orthogonal to each other, there was no complication from the vinyl groups and terminal alkynes on the POSS cage. The CHO-(VPOSS)-DIBO [72], containing three different “click” functionalities (aldehyde for oxime ligation, DIBO for SPAAC, and vinyl groups for TEC), is another important precursor for making multicomponent giant molecules. While oxime ligation is orthogonal to both SPAAC and TEC, the possible interfere between the latter two reaction is avoided by performing SPAAC before TEC in sequence, leading to one-pot preparation of single-tailed and asymmetric multi-tailed giant surfactants in a short time [72].

4. “Clicking” POSS cages for hybrid materials

4.1. Single “click” strategy

CuAAC has been widely applied to conjugate POSS with other functional molecular moieties [105] as well as polymers [22]. Conventional chain-end modification of polymers is usually suffered from the reduced reactivity, which impedes complete reaction and hampers further study of POSS-polymer hybrid materials. Facile and efficient approaches to POSS-containing giant molecules have recently been developed to address this problem using “clickable” POSS building blocks.

The simplest case is “clicking” one POSS nanoparticle onto polymers. This head-tail geometry resembles small-molecule surfactants, yet possesses amplified sizes comparable to block copolymers [21]. The so-called “giant surfactants” thus bridge the gap between small-molecule surfactants and block copolymers [21]. Although computational simulation has predicted many unconventional self-assembly behaviors [162–164], experimental studies have not been explored in depth until recent years, mainly due to difficulties in synthesizing well-defined model compounds. In their pioneer work, Zhang and Müller developed mono-alkyne and mono-azido functionalized POSSs and coupled them with azido- and alkyne-functionalized polymers, respectively, to give tadpole-shaped giant surfactants [98,126,148]. Similar approaches have also been applied to other giant surfactants with different tail properties (*e.g.*, hydrophilic [126,148] or hydrophobic tails [98,126], rigid tails [99], stimuli-responsive tails [97,100], or block copolymer tails [95,100] *etc.*). For example, a “clickable” fluorinated POSS cluster was functionalized with seven heptadecafluorodecyl side chains on its periphery (FPOSS) before the installation of “click” functionality. A series of FPOSS-containing giant surfactants were then prepared by subsequent CuAAC “click” reaction [61,165]. Notably, by varying the position of azide groups on polymer, “topological isomers” of giant surfactants with similar composition but distinct topology can be constructed [61] and their assembly exhibits remarkable sensitivity to molecular topologies [52]. For example, FPOSS-PS-*b*-PEO possesses three mutually immiscible blocks including the hydrophilic PEO block, the hydrophobic PS block, and the omniphobic FPOSS cage, which serves as a model multicomponent hybrid material for the study of self-assembly in solution [165]. At low water contents, it could self-organize into spheres and cylinders with a core-shell-corona structure, with FPOSS cages aggregated as core, PS blocks as shell, and PEO chains as corona (Fig. 8). A large variety of unconventional micellar morphologies, such as toroids, tadpoles, dumbbells, two-dimensional (2D) hexagonally patterned colloidal nanosheets, and laterally

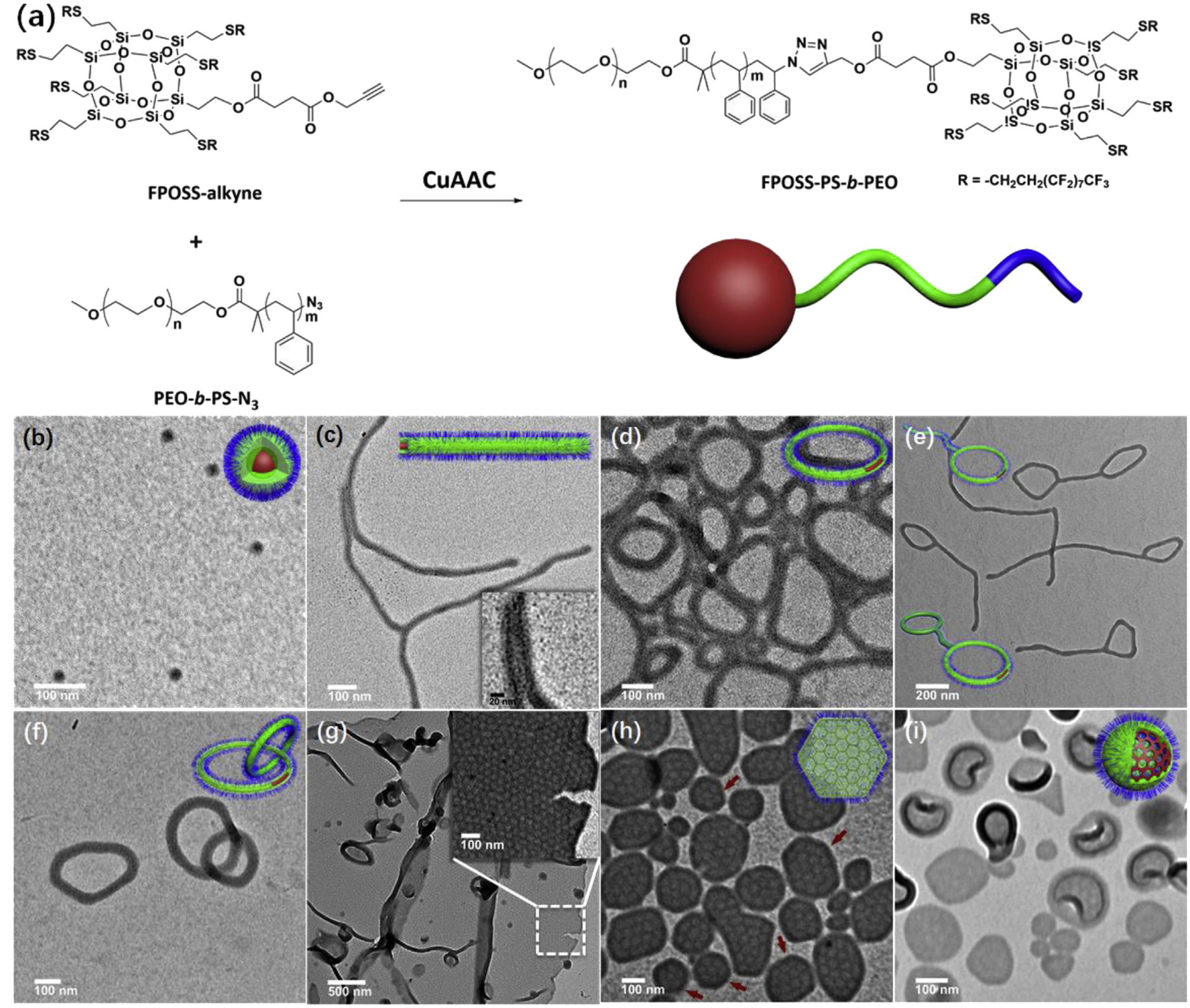


Fig. 8. "Click" synthesis of FPOSS-PS-*b*-PEO (a) and morphologies of the assemblies formed by FPOSS-PS-*b*-PEO at various stages: spheres (b), cylinders (c), toroids (d), tadpoles and dumbbells (e), interlocked toroids (f), 2D nanosheets (g, h), and laterally structured vesicles (i). The inset in (f) is an enlarged image of the area inside the white box. The proposed models are illustrated with different colors: FPOSS (red), PS (green), and PEO (blue) [165]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

structured vesicles sequentially formed with increasing water contents. Most interestingly, micrometer-sized thermodynamically stable 2D hexagonally patterned nanosheets with hexagonally connected FPOSS domains in a PS matrix covered by the PEO corona were observed, offering a new pathway toward "bottom-up" fabrications of 2D nanostructured sheets [165].

Analogous to small-molecule surfactants, giant surfactants include giant bola-form surfactants, giant gemini surfactants, giant multi-headed/multi-tailed surfactants *etc.* [21]. They can be readily prepared using rationally designed azido-functionalized polymer precursors. Giant bola-form surfactants are telechelic POSS-containing hybrid polymers. Zhang and Müller reported the syntheses of telechelic POSS-containing polystyrene using α, ω-diazido or dialkyne functionalized precursors via a combination of atom transfer radical polymerization (ATRP) and CuAAC click reaction [126]. A similar telechelic POSS-containing hybrid amphiphiles with hydrophilic poly (acrylic acid) (PAA) could self-organize into ellipsoidal aggregates with moderately uniform sizes in aqueous solution [128]. Zheng's group prepared a series of hepta (3,3,3-trifluoropropyl) POSS-capped polymer telechelics with PNIPAAm middle blocks [94,150]. The resulting hybrid polymer could self-assemble into physical hydrogels that shrink and release water upon increasing temperature, indicating the occurrence of volume phase transition [150]. A similar approach has been adopted by our group to prepare giant bola-form surfactants end-capped with two hydrophilic POSSs [53]. We have shown that hetero-functionalized asymmetric giant bola-form surfactants composed of PS middle block and two distinctly functionalized terminal POSS cages could be facilely prepared and could form a variety of different ordered structures in the bulk state with sub-10 nm [161].

POSS cages have also been attached onto polymeric backbones as side chains [101–104,127,129,149,154]. For example, Kuo and co-worker coupled multiple mono (benzyl azido) isobutyl POSS (BPOSS-N_3) onto the polymeric backbone of PBLG homopolymer or of PS-*b*-PBLG block copolymer [101,102]. It was found that the fraction of α-helical secondary structures increases in both cases after attaching BPOSS nanoparticles to their side chains. More interestingly, hierarchical self-assembly behaviors were also observed in both systems, involving the formation of a hexagonally packed cylinder with α-helical conformation of the POSS aggregates [101,102].

POSS scaffolds fully covered with azido/alkyne groups present an opportunity to fabricate POSS-cored nanoclusters with tunable surface properties in one-step CuAAC reaction. The N_3POSS derivatives are the most widely used precursors. All T_8- [84,106,107,134] T_{10}- and T_{12}-type [77,79] azide-functionalized building blocks have been reported with either soft or rigid linkers. A myriad of alkyne-functionalized moieties were incorporated onto the periphery of POSS cages in a modular way. For example, Yuan et al. used the N_3POSS building block to couple with alkyne-PEO and/or alkyne-PLLA via CuAAC to make homo- and hetero-arm star polymers exhibiting interesting solution self-assembly and crystallization behaviors [82,83]. Liu's group reported the preparation of quatrefoil-shaped star-cyclic PS possessing a rigid POSS core via a combination of ATRP and CuAAC reaction [84]. In addition, the versatility of octa-(3-azidopropyl) POSS as an important 3D nanobuilding block for efficient preparation of different hybrid nanoclusters with cubic symmetry has been fully demonstrated by several groups, which results in functional materials including POSS-RGD peptide octaconjugate [90], glyco-POSS conjugate [78,80,81], dye-labeled POSS-based photonic nanoclusters [78,81,91], and 4.2 nm-sized adamantyl nanocages [80]. On the other hand, T_8-N_3POSS with more rigid molecular structures (*e.g.*, with benzyl spacer between azido group and central cage) were synthesized by Kuo [92,106,107,134] and Ervithayasuporn's group [166], respectively. One of the promising applications of those rigid POSS compounds is to synthesize nucleobase-multifunctionalized nanobuilding blocks [134]. It was found that complexation of star-shaped adenine- and thymine-functionalized POSS could form a supramolecular network with lamellae structure via multiple hydrogen bonds [134]. Additionally, T_{10} N_3POSSs with D_{5h} symmetry (*i.e.* deca (3-azidopropyl)silsesquioxane) were also employed to construct functional soft materials including supramolecular dendrimers [79] and giant shape amphiphiles [77]. Notably, by controlling stoichiometry of N_3POSS, POSS nanoclusters with hetero surface properties were constructed in just two steps of CuAAC reactions, as developed by Chiara's group [77,81].

Like N_3POSS, alkyne-POSS precursors have also been designed and synthesized [85–88]. Hwang and co-workers used a T_8 alkyne-POSS to prepare star-like polymer hybrids using either “grafting-to” or “grafting-from” strategy with a combination of CuAAC reaction and RAFT polymerization [85]. Kuo's group prepared a multi-diamidopyridine-functionalized POSS nanocage (MD-POSS) via CuAAC, which can be further mixed with mono- or bis-uracil-functionalized PEO derivatives to form the spherical supramolecular structures [86]. Moreover, alkyne-POSS was also employed as the core to divergently synthesize peptide dendrimers as potential gene delivery carriers [88]. CuAAC has also been applied to construct POSS-containing macromolecules with complicated architectures, such as main-chain polymers [125] and star-like polymers [95,96,126]. For example, Zheng et al. prepared a POSS-containing main-chain copolymer via CuAAC condensation polymerization of dialkynyl-terminated oligoethylenes with diazido-functional T_{10} POSS, which exhibits many interesting physical properties including high glass transition temperature, high thermal stability, and extremely low surface energy [125].

TEC reaction offers a straightforward way to incorporate BPOSS-SH onto alkyne-containing polymers. For example, Lowe's group reported a general post-functionalization strategy of ring-opening metathesis polymerization (ROMP) polymers using different functional thiols including BPOSS-SH via radical TEC chemistry [157]. It represents an alternative way to hydrogenate the ROMP (co)polymer backbones [157]. Similarly, POSS-SH/X mixture developed by Jiang's group could further react with multi-acryloyl/-yne modified supporters (*e.g.* caster oil [132], nanopatterned hydrogel [133], hyperbranched polymer [159]) for generating functional soft materials through thiol-ene/thiol-yne “click” reactions. For instance, a one-step thiol-ene photopolymerization of POSS-SH/PEO (as reactive surfactants) and trimethylolpropane triacrylate (TMPTA, as a cross-linker) was conducted to prepare hybrid microcapsules with excellent thermal and mechanical performance. The superior ability to load both hydrophobic and hydrophilic dyes makes these microcapsules a promising vehicle in controlled dispersion and drug delivery [131].

TEC reaction is also particularly efficient for making POSS bioconjugations. The first study was exploited by Lee's group [50] by the addition of mannosyl and lactosyl thiobutyramides with VPOSS via TEC for POSS glycoconjugation. Later, Dondoni and co-workers [114,138,167] performed more systematic work on POSS-based octavalent glycoside and peptide clusters to further broaden its scope. Compared with CuAAC, TEC is a metal-free process that can be easily initiated by visible light with high efficiency, which is particularly useful in conjugation with unprotected sugar moieties such as sialic acid. The first sialylation of POSS was achieved via TEC addition between alkyl-tethered sialic acid thiol and VPOSS in a mixed solvent of DMF and THF [114]. A modest cluster effect of multiple sugar functionalized POSS was confirmed by Enzyme-Linked Lectin Assay (ELLA) of mannoside and glucoside-coated POSS clusters toward Concanavalin A. Moreover, the T_8 VPOSS has also been utilized to construct porous polymeric hybrid functional materials with large surface area [108,109,137]. The preparation process fulfills the “click” philosophy in two aspects: (1) one way is to use VPOSS and multi-functional thiols to develop the hybrid monolithic materials via the step-growth mechanism of TEC reaction [108]; (2) the TEC reaction can also be subsequently employed to tune the surface functionalities of formed nanoporous structure containing residual vinyl groups via reacting with various functional thiols such as thiolated PEG or thioglycolic acid [109,137]. The resulting porous organic–inorganic hybrids allows for a wide range of applications including extraction, separation, and catalysis. Moreover, SH-BPOSS can also be used for direct TEC/Thiol-Michael cross-linking fabrication of functional hybrid materials. For example, Jiang and co-workers reported a general and simple method to *in-situ* fabricate photocrosslinked polymeric vehicles during the co-assembly of SHPOSS and acrylated graft poly (ether amine) [124]. The resulting hybrid vesicles exhibit interesting thermo-responsive behaviors in aqueous solution, and could be utilized for controlling the dispersion of both hydrophilic and hydrophobic dyes in water. In addition, again starting from SH-BPOSS, Ellison’ group proposed a useful and environmentally friendly fabrication method via the integration of TEC reaction and simultaneous centrifugal technique to prepare inorganic-organic hybrid fibers with ultra-high POSS loading (about 80%) and well dispersion of the inorganic content [115]. The resulting fibers possessed tunable thermal and mechanical properties and were regarded as promising candidates for catalyst supports and filtration media under harsh conditions.

4.2. Double “click” strategy

POSS building blocks with two different “clickable” sites allow multiple functionalization using a combination of several click reactions. Based on the orthogonal nature of different reactions, the synthetic strategy could adopt either sequential or one-pot fashion. VPOSS-alkyne represents the first POSS-based "double-clickable" building block [54]. The alkyne group could conjugate with polymers of various chain topologies (*e.g.* linear, cyclic, and hyperbranch) [54,119,120] and chemical compositions (*e.g.* hydrophobic and hydrophilic) [54,161], while vinyl groups on POSS periphery allow the installation of different functional thiols via subsequent TEC reaction. This sequential "click" methodology offer a simple and tunable way for systematic tuning of the molecular parameters of XPOSS-polymer giant surfactants with complex structures and various composition. The self-assembly behaviours of these giant surfactants possesses a duality of both small-molecule surfactants and block copolymers in the bulk and solution [51,52]. They are attractive by virtue of their capability to construct supramolecular structures with sub-10 nm feature sizes [52].

Again starting from VPOSS-alkyne, multi-head/multi-tail giant surfactants can be achieved in a modular and efficient fashion following the CuAAC approach with the help of "click" adaptors (will discussed in the next section), providing an easy access to a family of giant surfactants with precisely-defined chemical structures and fine-tuned interactions for a systematic study of structure–property relationships [53]. Those molecules usually possess one or more types of "clickable" functionalities or masked "clickable" groups (*e.g.*, halogen groups can be regarded a masked "azido" group by subsequent nucleophilic substitution with NaN_3). As an example, it is very convenient to convert a mono-azido functionalized PS to a novel precursor with two PS chains and two azide groups, leading to gemini giant surfactants consisting of two hydrophilic POSS and two PS tails [53]. Following similar approach, the multi-headed giant surfactant which is composed of three hydrophilic POSS cages tethered at one end of a PS can be readily prepared by simply varying the molecular structure of "click" adaptors [53].

Taking advantage of the modular synthesis of POSS-polymer conjugates, we prepared several series of giant surfactants with one hydrophilic POSS head and different numbers of PS tails of a statistically identical length (the number of PS tails ranges 1 to 4). Using these four sets of giant surfactant samples (DPOSS-mPS_n, m = 1 to 4), we recently revealed an interesting mechanism to construct unconventional spherical supralattices induced by variations in macromolecular geometry [168]. With increasing number of PS tails (m = 3 and 4), not only were observed the shifted volume fraction boundaries between microphase separated nanostructures, but also unconventional Frank-Kasper A15, Frank-Kasper σ, and a dodecagonal quasicrystal (DQC) supramolecular structures between the common Hex and BCC phases (Fig. 9). Molecular dynamic simulation results also confirmed the geometry-induced structural evolution towards unusual spherical supralattices in giant surfactants [168]. These results further highlighted the critical significance of macromolecular geometry in dictating the formation of nanostructures via self-assembly of amphiphilic polymers.

In addition, a variant of VPOSS-alkyne with shorter linkers (such as esterification product of VPOSS-OH and propiolic acid) has also been employed to construct a family of giant tetrahedra using similar synthetic strategy (Fig. 10) [121]. We envisioned that controlled symmetry breaking of giant tetrahedra could lead to precise positional interactions and create unconventional structures via selective assembly in solid state. For example, a giant tetrahedron, consisting of three BPOSS and one hydrophilic POSS (i.e. DPOSS, APOSS, HPOSS) at its vertices, first self-organizes into a crystalline lamellar structure with a frustrated 3-layer packing

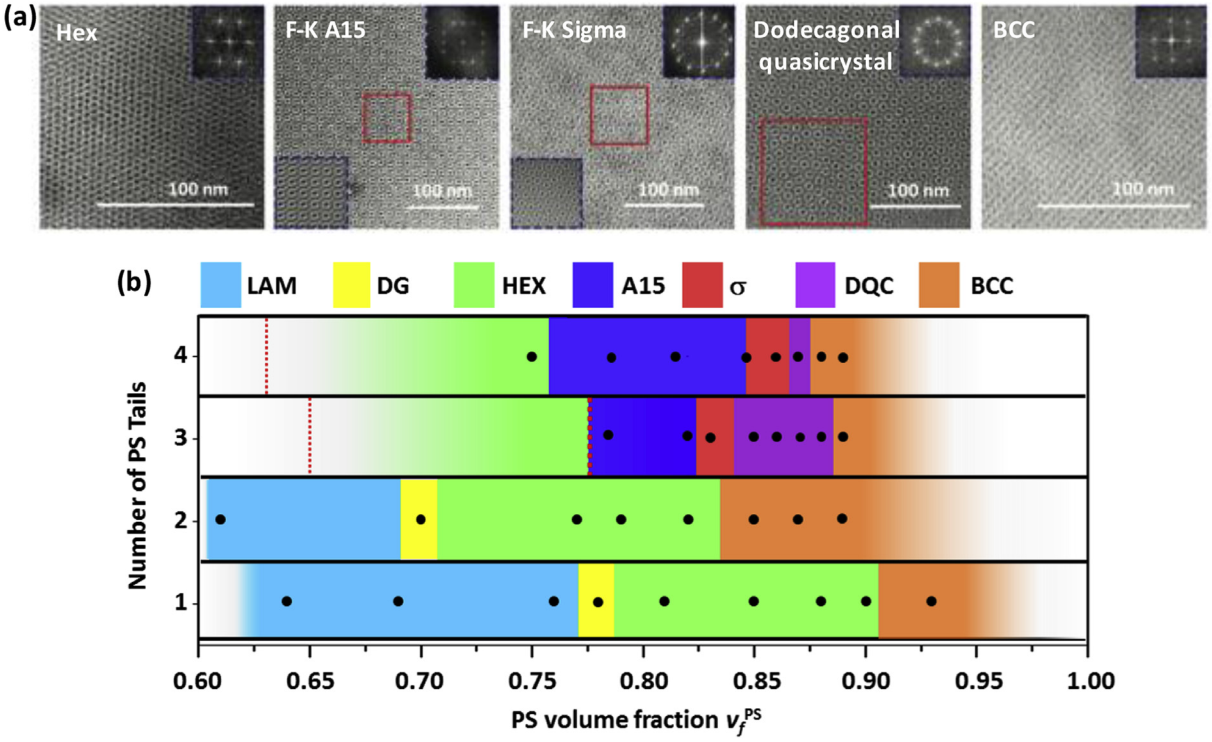


Fig. 9. (a) Representative bright-filed TEM images of DPOSS-$4PS_n$ samples showing (from left to right) Hex, Frank-Kasper A15, Frank-Kasper σ, DQC, and BCC phases. (b) Experimental phase boundary diagrams of DPOSS-mPS_n (m = 1 to 4) giant surfactants with different molecular geometry [168].

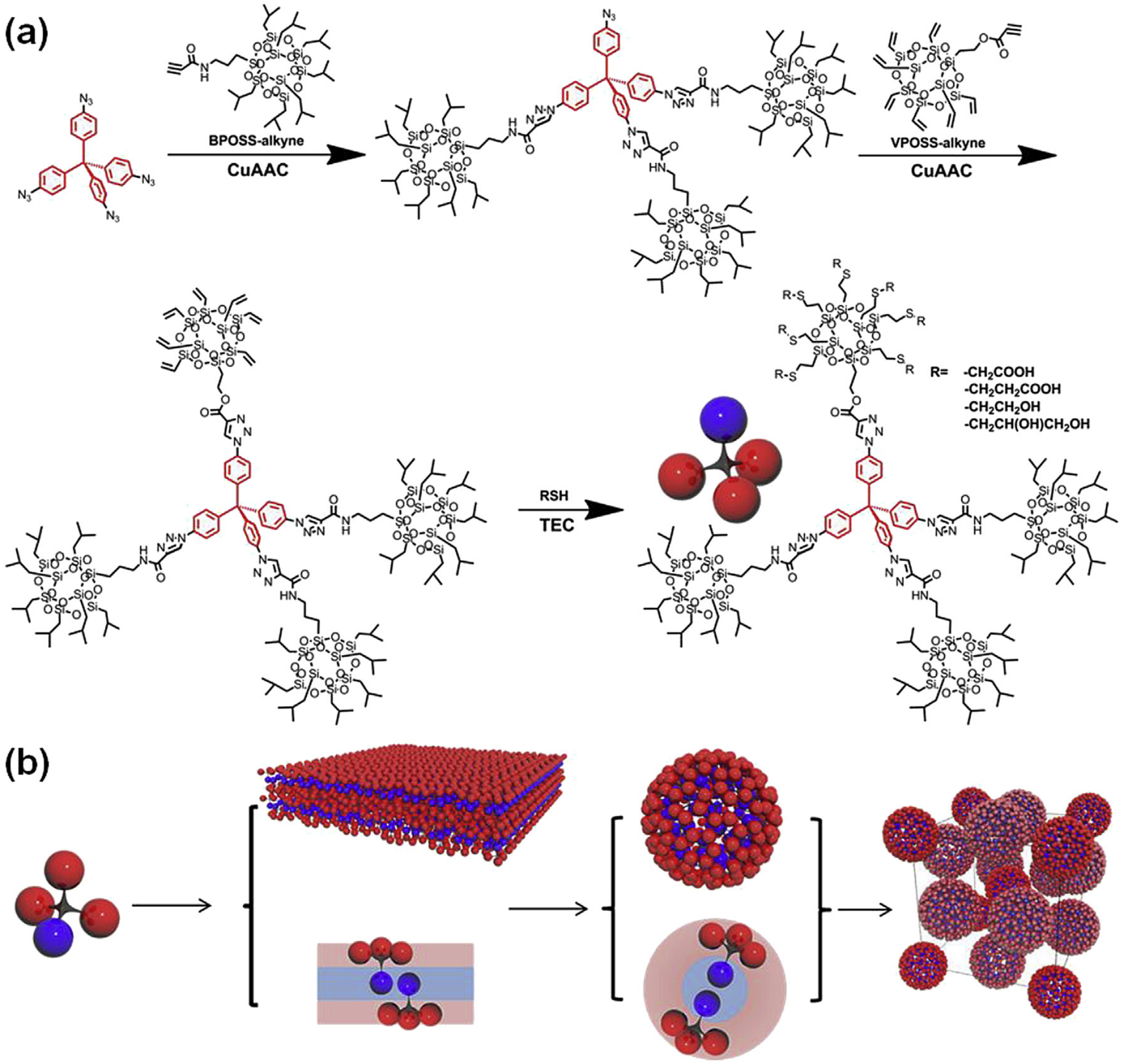


Fig. 10. Synthesis (a) and self-assembly mechanism (b) of giant tetrahedron containing three BPOSSs and one hydrophilic POSS [121].

scheme owing to the crystallization of BPOSS cages that usually prefers flat interfaces. After annealing near the melting temperature, supramolecular spheres with hydrophilic POSS cages as the core and hydrophobic BPOSS cages as the shell were assembled. These spherical building blocks further packed into a Frank-Kasple A15 lattice that is normally found in metal alloys [121]. In this lattice, two supramolecular spheres with 12- and 14-folded coordination environments are formed with different spherical sizes, suggesting that the formation of this Frank-Kasper A15 supramolecular lattice must be associated with the deformability of the selective-assembled spheres and shape polydispersity.

4.3. Triple "click" strategy

The synthetic strategy involving triple, or even more, kinds of "click" reactions offers well-controlled molecular heterogeneity, including chemical composition, functionality, and topology. An important example was recently demonstrated by our group in precisely arranging multiple POSS nanoparticles along the chain (Fig. 11) [135]. Building blocks with distinct surface functionalities, so-called DIBO-(XPOSS)-CHO where X describes periphery functional groups like vinyl (V), isobutyl (B), fluoroalkyl (F), and chloroalkyl (Cl), were attached onto polymeric backbone in a designed manner similar to playing with Legos. It offers a modular way to tune the POSS number, surface functionality, and chain topology. These molecular parameters were found to impact tremendously their self-assembled hierarchical structure formation in the bulk (Fig. 12) [135]. Similar effects were also observed in their self-assembly behaviors in solution [136].

4.4. Iterative/fractal synthesis enabled by "click" adaptors

"Click" chemistry-based iterative/fractal synthetic strategy are particularly useful for constructing complex macromolecular structures of POSS-contained giant molecules. Note that kinds of macromolecular parameters, such as molecular weight, nanoparticle surface functionalities, polydispersity, weight fraction of heads/tails, asymmetry of head/tail could be independently controlled and systematically varied in minimum steps. "Click" adaptors, describing a class of small molecules that can facilely convert one "click" functionality to another one or to extend the total number of "clickable" sites (as shown in Fig. 12), were regarded as useful tools for iterative/fractal synthesis.

Those molecules usually possess one or more types of

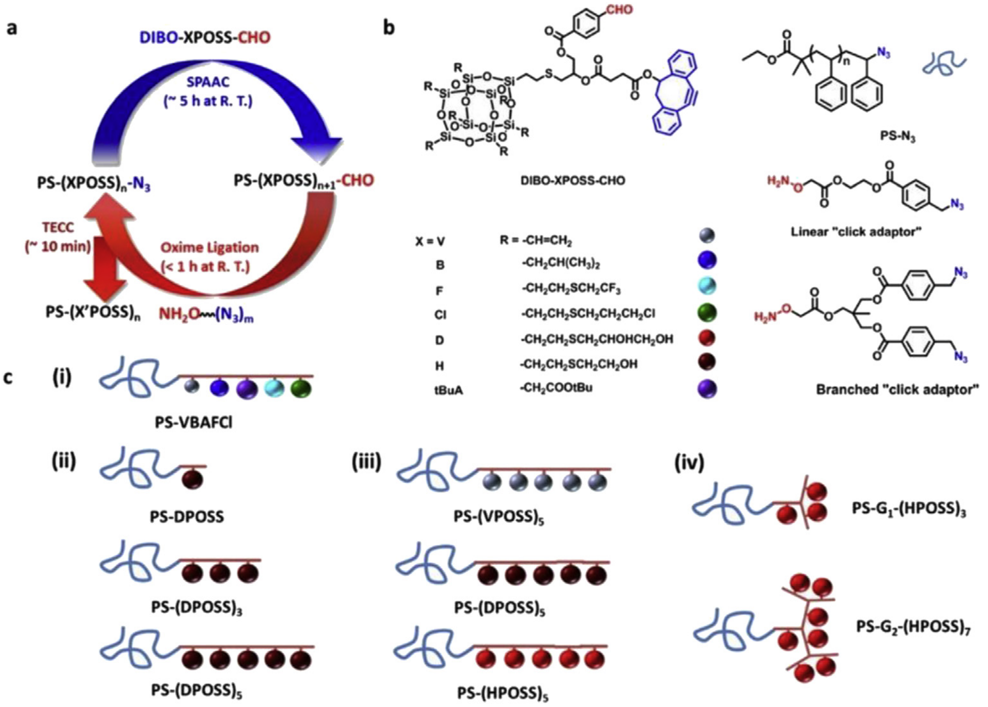


Fig. 11. Synthetic routes and representative macromolecular design of giant molecules with controlled heterogeneities including POSSs in a designed sequence, tunable numbers, tunable functionalities, and topologies [135].

"clickable" functionalities or masked "clickable" groups (*e.g.*, halogen groups except fluoride can be regarded masked "azido" groups since they can be easily converted to azide by nucleophilic substitution, Fig. 13) [21,53,73,135]. In general, "click" adaptors are very useful for further expanding the scope of POSS-based giant amphiphiles during both sequential and one-pot synthetic process. For example, we have successfully employed this concept to construct multiheaded giant surfactants by using molecular "click" adaptor **1** [53], which consists of one alkyne group and three bromo groups. After the first step CuAAC reaction between azido-terminated polymers (i.e. PS-N_3) with adaptor **1**, the rest three bromo groups can be converted into azido groups, resulting in a PS chain end with three "clickable" functionalities. The second step CuAAC reaction can then be performed to conjugate three VPOSS cages at the end of PS chain, leading the formation of multiheaded giant surfactant precursors for further TEC head modification. Taking advantages of this "click" adaptor, all of the involved reactions are "click"-type, making synthesis efficient, modular, and convenient. By simply varying the molecular structure of "click" adaptors, the above strategy enables the systematic preparation of giant molecules with various macromolecular architectures. In addition, "molecular click adaptor" **3**, contains two functional groups of completely orthogonal "click" reactivity (*e.g.* azido group for CuAAC/SPAAC, and aldehyde for oxime ligation, respectively), facilitating the efficient transformation of one "click" functionality to the other [73]. It was successfully applied into the fractal development of asymmetric giant gemini surfactants with tunable chemical compositions by preparing "clickable" giant surfactant precursor for the subsequent tandem synthesis [73]. Moreover, note that specifically designed "click adaptor" (*e.g.* molecule **4**) could introduce the branch geometry during the click functionality transformation process, directly offering a simple way to tune the architectures of resulting hybrid macromolecules [135,136]. By using such "click" adaptors, all "click" products can be used as new "clickable" building blocks subject to further iterative or fractal synthesis, greatly adding to the complexity and sophistication of the giant molecules that can be synthesized.

5. Discussions

5.1. "Click" chemistry in reality

Combined utilization of multiple "click" chemistry allows for the preparation of POSS-based hybrid materials with complex compositions and architectures. Although several "click" reactions have been developed and widely used, they only share some of the features of the ideal click chemistry. In other works, they are not always perfect in reality. Therefore, the integration of two or more "click" reactions in sequential or simultaneous fashion remains a challenge (Fig. 14). To select the proper reactions and arrange the right sequence of reaction, one should consider the following issues: (1) the stability of related "clickable" functional groups under other "click" experimental conditions and (2) potential cross reactions between functional groups. The concern arises because in reality, side reactions are often inevitable, such as the instability of aldehydes [169], the oxidation/reduction of thiols especially in the presence of copper catalysts [170], and the cross-reaction between alkyne and thiols [171,172]. Minor structural variations may also affect the reactivity and selectivity of the "click" functionalities. Although "click" reactions are supposed to be ideally orthogonal, the number of strictly orthogonal reactive pairs is still limited. At the current stage, the majority of synthetic routes towards multifunctional POSS-based hybrid materials mainly relies on the sequential "click" approach, while only a few examples have been reported by using the simultaneously one-pot method.

Considering the above issues, only accurate design of appropriate reaction conditions and orders enables the successful integration of different "click" methodologies. It means that we need to carefully select the pairs of "click" reactions that do not interfere

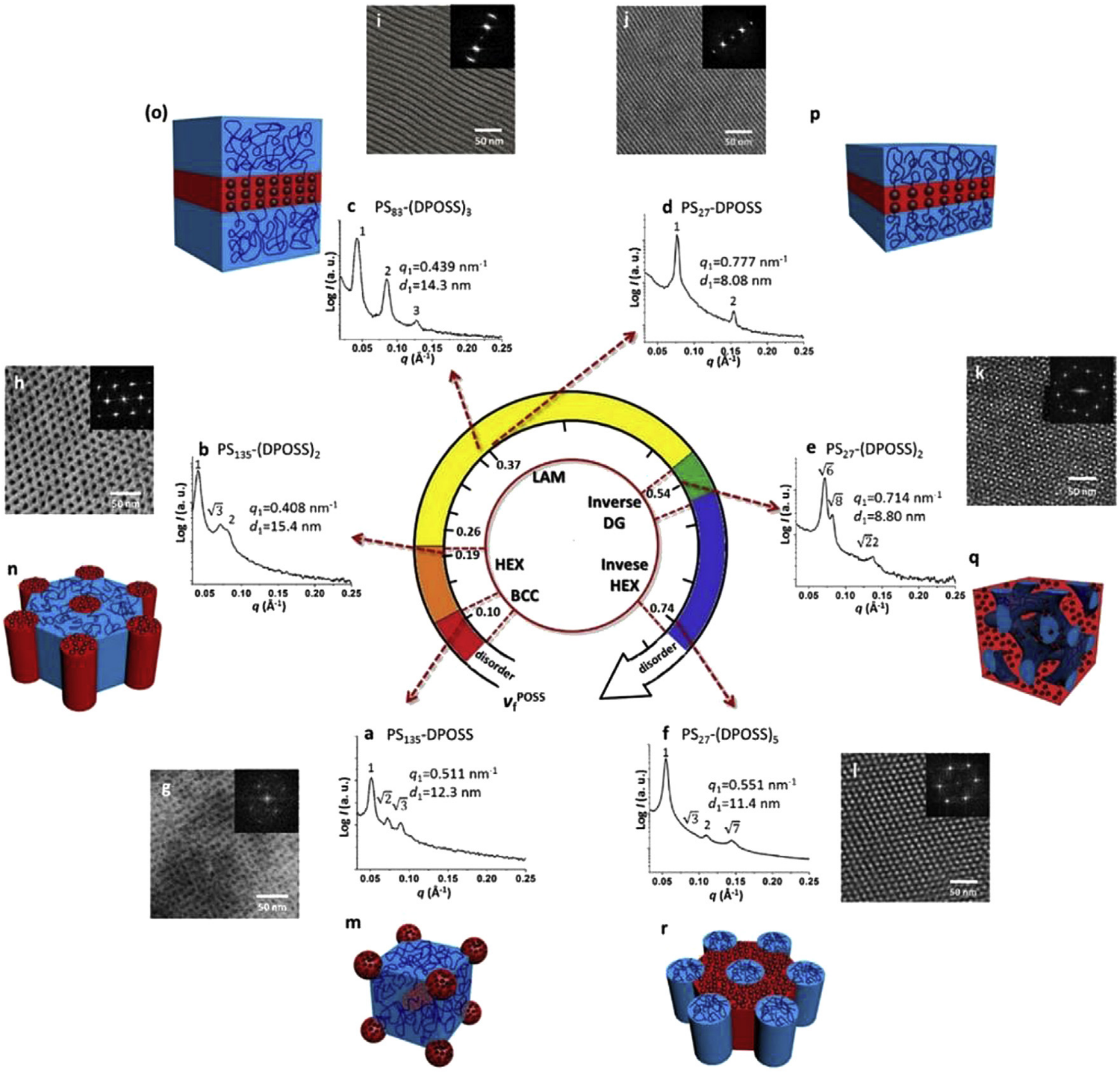


Fig. 12. Self-assembled supramolecular structure phase diagram of PS–POSS giant surfactant in the bulk [135].

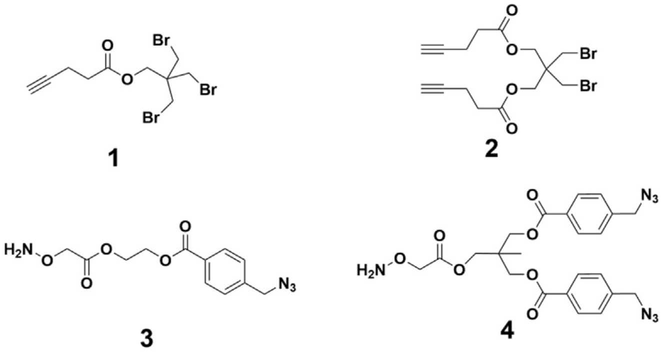


Fig. 13. Chemical structure of several established "click" adaptors [53,73].

with each other under certain conditions to facilitate the sequential reactions. For example, starting from VPOSS-alkyne to prepare XPOSS-polymer conjugate [54], the CuAAC reaction has substrate-selectivity for terminal alkyne (not interfere with vinyls), while the radical-mediated TEC reaction does undergo with both alkyne and vinyls. The combination of these two reactions should thus be CuAAC reaction first, followed by the TEC reaction. Furthermore, a triple "click" chemistry methodology has also been similarly proposed by using sequentially performed SPAAC, CuAAC, and TEC reactions, as discussed in section 4.3 [39]. Particularly, with the increasing demands on the total number of components in the multifunctional POSS materials with more complex chemical compositions and molecular architectures, more "click" reactions should be involved in the whole synthetic route in an appropriate order. In a recent example, four types of consecutive "click" reactions were performed for the precise and modular preparation of macrocyclic giant surfactants tethered with two different POSSs at distinct ring locations (Fig. 15) [40]. Benefited from the distinct chemical reactivity first between cyclooctyne and terminal alkyne in the absence of Cu(I), and second between activated enes and vinylsiloxanes without radical initiators, we extended the above approach to a sequential multiple "click" strategy involving sequentially performed SPAAC for bimolecular homobifunctional ring closure, CuAAC for POSS-polymer conjugation, thiol–Michael addition and TEC reaction for POSS surface functionalizations.(Fig. 15). Recently, echoing the structural evolution and increasing sophistication of giant surfactants via different combined sequential "click" methodologies (CuAAC/TEC

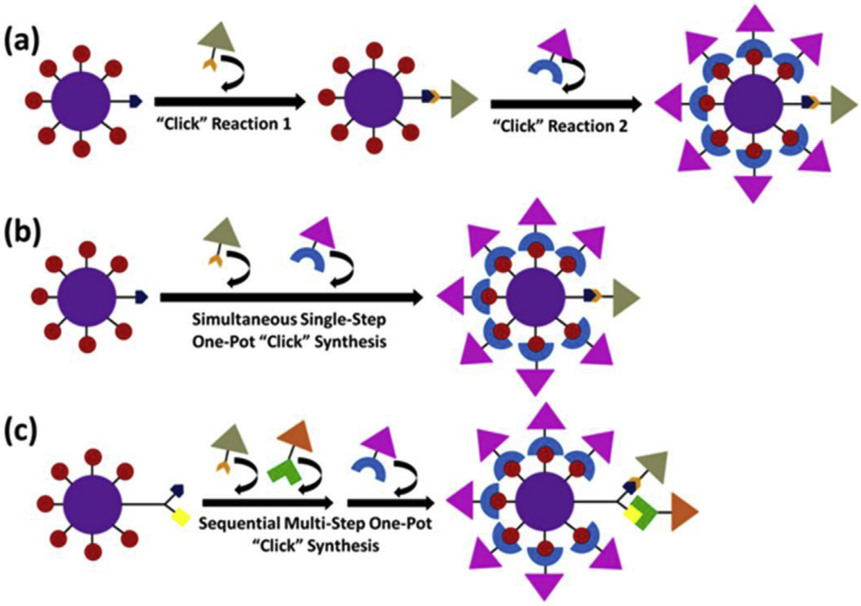


Fig. 14. Illustration of the specific synthetic methods using combined "click" methodologies toward POSS-based complex macromolecular structures: (a) sequential click approach [54], (b) simultaneous single-step one-pot synthesis [72], and (c) sequential multi-step one-pot orthogonal assembly [72].

[53–55,119,120], CuAAC/thiol–Michael [68], SPAAC/TEC [40], TEC/CuAAC [61], oxime ligation/CuAAC [77], SPAAC/CuAAC/TEC [39], SPAAC/CuAAC/thiol–Michael/TEC [40]), we have develop a library of POSS-based giant surfactants in analogy to their small-molecule counterparts, such as giant surfactants [54,61,68,77], giant lipids [119], giant gemini surfactants [55], giant bolaform surfactants [53], multi-headed/multi-tailed giant surfactants [39,53], and macrocyclic giant surfactants [40,120]. This series of giant surfactants denotes an evolution toward complex macromolecular structures yet with increasingly facile synthesis.

In addition, fulfilling the sequential "click" philosophy, Gao's group also proposed a general all-"click" chemistry methodology involving consecutive TEC, Menschutkin, and CuAAC reactions, to construct precisely-defined water-soluble T_8 POSS derivates with a large variety of functional groups on the surface (Fig. 16) [59]. The whole synthetic process is rapid, efficient, reliable, and controllable. It has also been observed that the resulting amphiphilic POSSs with long alkyl chains exhibit promising host-guest encapsulation properties due to their unique octopus-like nanostructures and relatively big cavities [59].

Although it is more difficult to use many "click" reactions in an orthogonal manner from one common building block, the one-pot synthesis offers many attractive advantages over individual reactions including minimum setup, short reaction time, easily scalable, and less work-up. Since two or more reactions are simultaneously accomplished in a single step or in one-pot, there is no need to isolate the intermediates, reducing the time and workload as well as increasing the overall yields. Such promising features inspire us to specifically design and synthesize two important precursors, VPOSS-CHO and CHO-(VPOSS)-DIBO, for cascading one-pot synthesis of POSS-based giant surfactants under mild conditions [72]. Notably, the former consists of two "click" groups of excellent orthogonality (vinyl for TEC and aldehyde for oxime ligation), enabling simultaneous one-pot synthesis of a single-tailed giant surfactant (Fig. 17a), while the latter only allows a sequential multi-step one-pot reaction (Fig. 17b). Compared with sequential "click" approach, it is truly advantageous in terms of simplified procedure (single step *vs.* multiple steps), reduced reaction time (0.5–2 h *vs.* one or several days), and increased yields (~85% *vs.* ~ 50%–60%) [39,54,72]. Moreover, this facile one-pot "click" synthetic strategy can be repeated performed to facilitate a tandem "fractal" synthesis of diverse, complex POSS-based giant surfactants from the modular building block, CHO-(VPOSS)-DIBO [73]. The whole synthetic process only takes an impressive two steps in less than 5 h for constructing a series of asymmetric giant gemini surfactants. More work on the development of new one-pot strategy is highly desired.

5.2. Reflections: "to click or not to click"

Click chemistry provides an efficient approach to construct POSS-based hybrid materials, enabling precise controls on architectures, compositions, and other molecular parameters. It, however, is not necessarily always the best choice [173]. The preparatory work such as the installation of "clickable" groups onto both POSS building blocks and other segments may compromise its efficiency. The removal of excess starting materials, for example polymers, is sometimes nontrivial. In addition, it remains a challenge to prepare uniform POSS-based giant molecules with molecular precision in a rapid and efficient process, especially when the molecular weights are exceedingly high [174]. "Click" approach might be inadequate in this case. Moreover, for the preparation of most POSS-based insoluble crosslinking systems, only simply washing, instead of complex operation steps for purification, is needed. In those cases, "click" chemistry can not represent obvious advantages compared with other kinds of efficient coupling reactions, either [173].

The advent of controlled/living polymerization techniques, such as ATRP [57], reversible addition-fragmentation chain transfer (RAFT) polymerization [150], and ring opening polymerization (ROP) [56,57], has rendered a much easier "grafting-from" preparation of well-defined POSS based hybrid materials, starting from proper functional initiators or chain transfer agents. For example, star-like PS and poly (methyl methacrylate) (PMMA) could be grown from T_8 POSS-based multi-initiators POSS-$(Br)_8$ using ATRP [84,175,176]. Hwang et al. have also utilized POSS-based chain

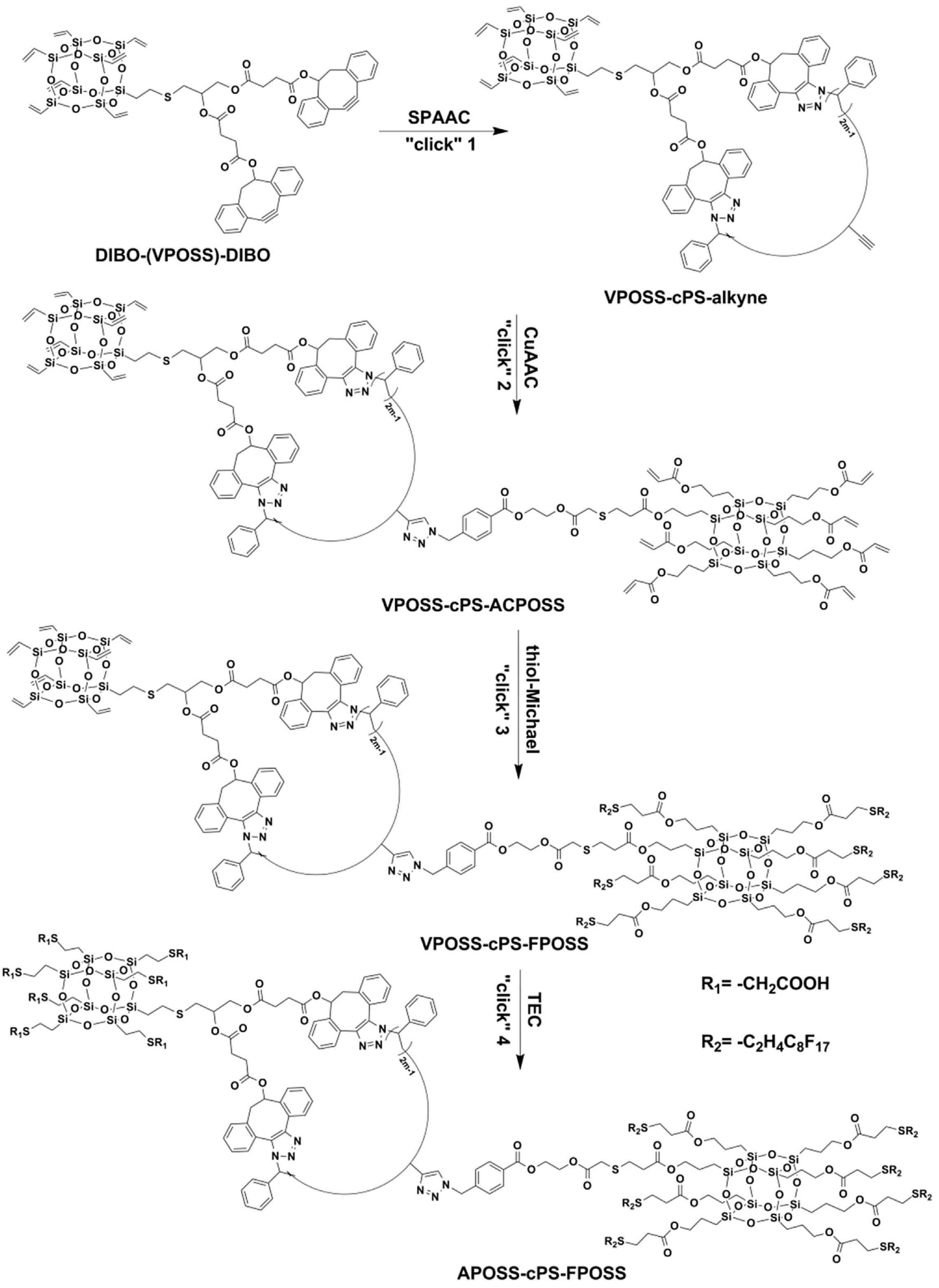


Fig. 15. Synthetic strategy based on four consecutive "click" reactions towards macrocyclic giant surfactants [40].

transfer agent to prepare star-like PMMA with POSS core by RAFT polymerization [85]. Our group reported a facile approach to synthesize POSS based giant surfactants using ROP [56]. A poly (L-lactide) (PLLA) chain was grown from VPOSS-OH with controlled molecular weight and narrow polydispersity. This method was further extended to prepare giant surfactants with complex architectures [57]. Using homo-bifunctional macroinitiators with two hydroxyl groups or bromoisobutyryl groups (VPOSS-diOH or VPOSS-diBr), POSS based giant surfactants with two symmetric poly (ε-caprolactone) (PCL) or PS tails were achieved by ROP and

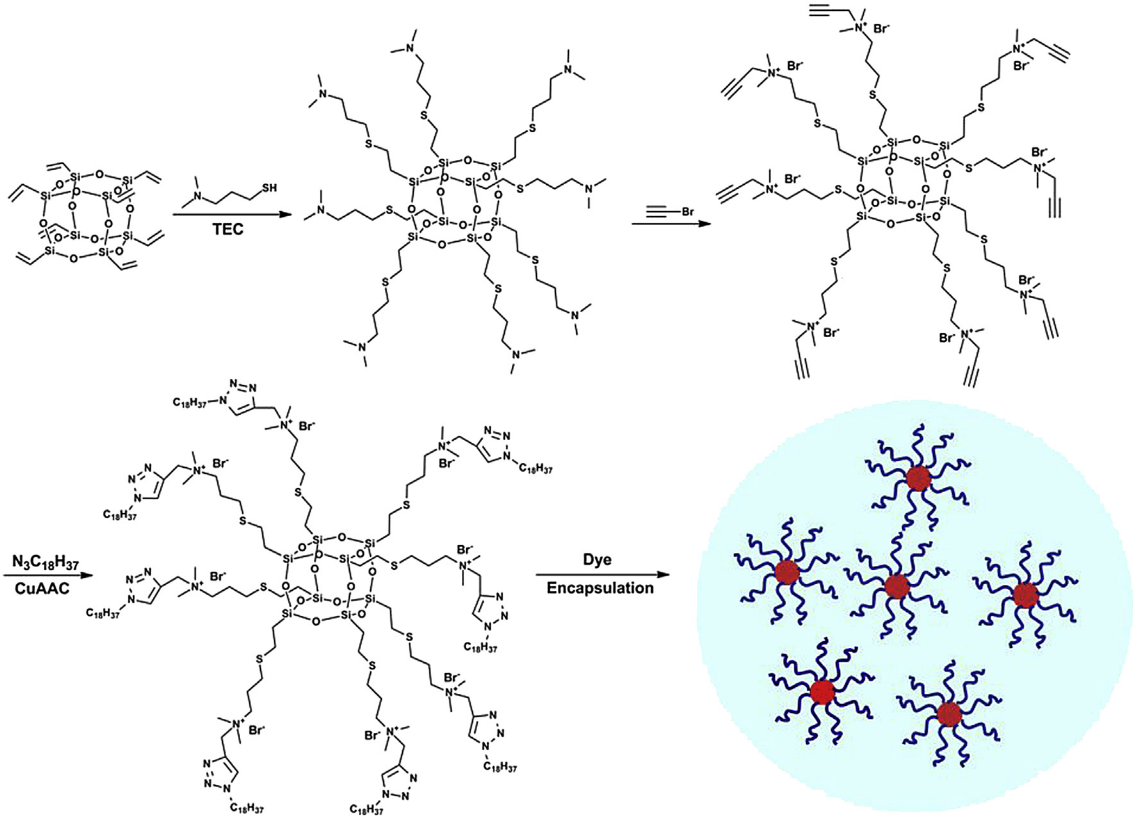


Fig. 16. Sequential synthesis of octa-alkyl chain-functionalized POSS and its application for dye encapsulation [59].

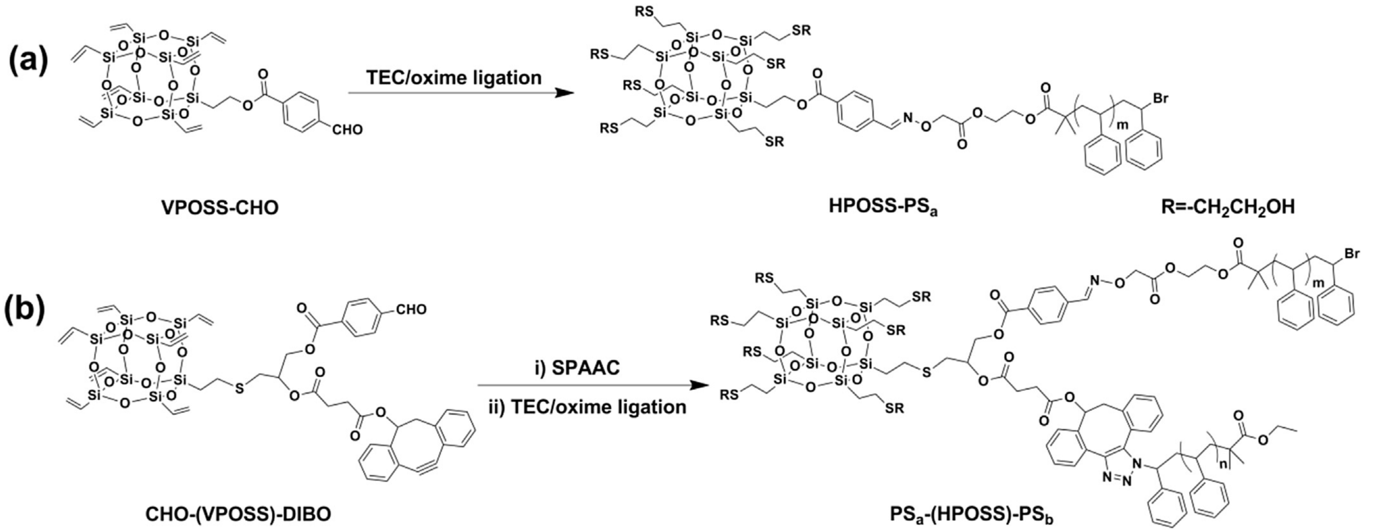


Fig. 17. One-pot synthesis of two kinds of POSS-Based giant surfactants via (a) simultaneous single-step one-pot reaction, and (b) sequential multi-step one-pot orthogonal synthesis [72].

ATRP, respectively [57]. A combination of these two processes with a hetero-bifunctional macroinitiators bearing a hydroxyl group and a bromoisobutyryl group affords tethered chains with asymmetric tail compositions (*e.g.*, one PS tail and one PCL tail) [57]. It is worth noting that in these “grafting-from” examples, monomers can be readily removed by repeating precipitation; whereas column chromatography or even fractionation might be required to remove excess polymer precursors when functionalized polymers were “clicked” onto POSS nanoparticles.

On the other hand, hydrosilation reaction also offers a useful way to modify hydrosilyl/ene group contained POSS building blocks with many functional groups due to its high efficiency and tolerance to various functionalities in the presence of Karstedts' catalyst [51,177]. Moreover, electrostatic interaction promoted association and reaction provides an effective solution to drive reaction to completion even for ligands of high molecular weights. Our group has developed a new approach for the preparation of well-defined, eight-arm star polymers via the addition of poly (styryl)lithium to octavinylPOSS in benzene, which proceeds rapidly to completion within 5 min for molecular weight of each arm up to 33 kg/mol [174]. It has a strong bias toward completion even at substoichiometric ratios. With stoichiometry control, this reaction can be utilized to prepare POSS based giant surfactants with single polymer tail [51], or block copolymer tails [57]. Although it is not defined as a click reaction, it could be a highly efficient reaction under certain circumstances. More importantly, it produces a very simple and inert Si-C bond which has minimum impact on the materials' properties. This is in contrast to CuAAC or SPAAC where a huge triazole linker is produced.

Additionally, complex hybrid macromolecules are best constructed by a combination of "click" chemistry and other efficient chemical transformations [26]. For example, Liu's group reported the preparation of quatrefoil-shaped star-cyclic PS possessing a rigid POSS core via a combination of ATRP and CuAAC reaction [84]. Since TEC might be the most efficient approach to install functional groups onto POSS head, the integration of TEC and controlled/living polymerization provides modular and efficient ways to synthesize POSS-based giant surfactants with diverse head surface chemistry [56,57]. In this sense, proper choice of methods based on the molecular design could promote the efficiency of syntheses. One should consider both the efficiency of linking and the minute difference of the resulting molecules. To click or not to click, this is a critical question. The best answer would finally be a balance between materials performance and synthetic ease.

6. Summary and perspective

"Click" chemistry has been a central topic in the recent innovation in rational design and facile synthesis of POSS-based functional hybrid materials. Combined utilization of multiple "click" reactions and other efficient chemical transformation enables expedited synthetic process with minimum number of reaction steps and convenient purification procedures. There is also no need to use large excess of reagents to drive reaction to completion. For broader implementation in hybrids materials with desirable macroscopic properties, future efforts toward several distinct directions are necessary. Firstly, POSS building blocks with multiple "clickable" groups are highly desired precursors, especially those multi-functionalized regio-isomers. Secondly, it is necessary to introduce new types of "click" reactions into the horizon to further improve and optimize the current synthetic methodology. Several ideal features are especially desired: it must be orthogonal to current used ones with controllable, stimuli-responsive reactivity, and it must be able to bridge the gap between synthetic and biologic macromolecules. Finally, although many kinds of multiple "click" functionalization methodologies have been developed, only very limited cases of POSS hybrids were related to multi-"functions" for practical applications. Decreasing the cost of POSS and rediscovering the "useful" properties of silsesquioxane cage seem to be inevitably for pushing POSS-based functional hybrid materials in practical usages. Overall, with the development of "click" methodologies as well as new "clickable" POSS building blocks, more kinds of POSS-based funtional hybrids materials will be designed, synthesized and fabricated for diverse applications. The frontier remains widely open and the entrance is limited only by ones' imagination.

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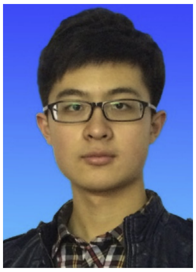
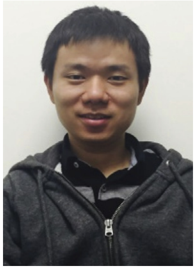
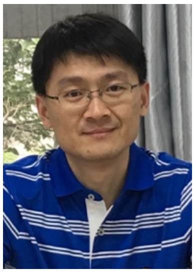


Yuan Zou completed his BS degree in polymer science and engineering from Sichuan University in 2017, under supervision by Professor Yiwen Li. He will continue to his MS study in Prof. Li's group in fall, 2017. His current research interests focus on the synthetic melanin and functional polycatechol nanomaterials-based novel catalysts.



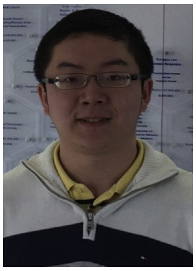
Zhao Wang was born and raised in LiYang, China. He earned his BS degree in the Department of Material Science and Engineering at East China University of Science and Technology and MS degree in the Department of Polymer Science at University of Akron working with Prof. Stephen Z.D. Cheng. In 2013, he moved to San Diego, The University of California San Diego for his PhD study, working with Prof. Nathan Gianneschi mainly on bio-related polymeric materials. In July 2017, Zhao moved to Northwestern University as a visiting predoctoral fellow.



Kan Yue obtained his bachelor degree in chemistry from Peking University in 2008. He joined the Department of Polymer Science of the University of Akron and received his Ph.D. degree in Polymer Science in 2013 under the supervision of Prof. Stephen Z. D. Cheng. After postdoctoral training at the University of Akron and Brigham Women's Hospital, he joined the South China Advanced Institute for Soft Matter Science and Technology (AISMST) of South China University of Technology as a principle investigator in January 2017. His research focuses on the study of self-assembling polymers and the development of novel functional materials.

Mingjun Huang grew up at Jiangxi Province in middle part of China. After receiving his B.S. degree majoring in Chemistry in Peking University, he continued to pursue the Ph.D degree in the Department of Polymer Science at the University of Akron (UA) from 2010 to 2015, under the supervision of Dr. Stephen Z.D. Cheng. His primary research interests in UA focused on highly efficient synthesis of hybrid giant molecules combing controlled/living polymerization and "click" reactions and self-assembly behavior studies of hierarchical mesophases at nanoscale. From June 2016, he joined the group of Prof. Jeremiah Johnson as a joint postdoctoral fellow, where he is exploring interesting polymer chemistry and energy materials studies.

Hao Liu comes originally from Chongqing, China. He received his B.S. in Chemical Engineering from the University of Science and Technology of China (Hefei, Anhui) in 2010 and his Ph.D. in Polymer Science from the University of Akron in 2015. He is currently performing postdoctoral work in the Department of Chemistry at the University of California, Berkeley. His expertise lies in the field of nanomaterials syntheses, characterization and catalytical applications, focusing on the precisely-defined molecular nanoparticles and nanoclusters.



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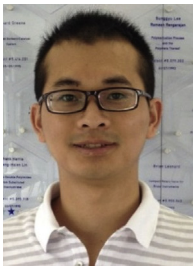
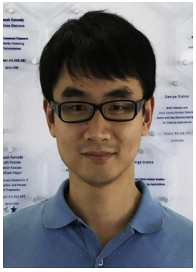
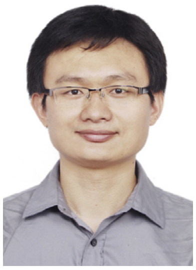


Zhiwei Lin received his B. S. degree in Polymer Science and Engineering and M. S. degree in Material Science and Engineering at Beijing University of Chemical Technology in 2008 and 2011. He then joined Department of Polymer Science at the University of Akron and received his Ph.D. degree in August 2016. He continued at the University of Akron for his postdoctoral research for one year, before joining Prof. Oleg Gang's research group at Columbia University as a postdoctoral fellow in September 2017.



Wei Zhang received his B.S. degree in Chemistry at Peking University in 2011. He then joined Department of Polymer Science at the University of Akron as a graduate student and received his Ph.D. degree in December 2016. After he continued his postdoctoral research at the University of Akron for 9 months. His current research interests are focusing on synthesis of sequence precise macromolecules and study their self-assembly. He is also interested in organic/polymeric semiconducting materials and biopolymeric materials. He will move to Harvard Medical School as a postdoc in September 2017.



Wen-Bin Zhang received his B.S. in chemistry from Peking University in 2004 and his Ph.D. in Polymer Science from the University of Akron in 2010 under the supervision of Prof. Stephen Cheng and Prof. Roderic Quirk. He stayed in Prof. Cheng's group for one more year before a second postdoc at California Institute of Technology with Prof. David Tirrell. He joined the faculty of Peking University in August 2013. His current research interest focuses on combining both the design principles and unique motifs of synthetic polymers and biopolymers for the development of precision macromolecules toward advanced functional materials.

Stephen Z. D. Cheng received his Ph.D. degree at Rensselaer Polytechnic Institute at Troy, New York, in 1985. His research interests are in the area of chemistry, physics, and engineering of polymers and advanced functional materials including ordered structure, morphology, phase transition thermodynamics, kinetics, and molecular motions. His recent interests in particular are focusing on nanohybrid materials with different molecular chemical structures and physical topologies, architectures, and interactions and their assemblies in the bulk, solution, and thin films. He is also active in developing researches of conducting polymers, photovoltaics, polymer optics, and photonics. Stephen Z. D. Cheng currently holds the R. C. Musson & Trustees Professor and serves as the Dean of the College of Polymer Science and Polymer Engineering at the University of Akron. He is the recipient of Presidential Young Investigator Award (1991), John H. Dillon Medal (APS, 1995), Mettler-Toledo Award (NATAS, 1999), TA-Instrument Award (ICTAC, 2004), PMSE Cooperative Research Award (ACS, 2005), Polymer Physics Prize (APS, 2013), SPSJ International Award (Society of Polymer Science, Japan, 2017) and other awards and recognitions. Cheng has been a Fellow of AAAS and APS and an Honorable Fellow of Chinese Chemical Society. He has been elected as a member of the National Academic of Engineering of US (2008).