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# Facile synthesis and linker guided self-assembly of dendron-like amphiphiles☆

Bo Ni[a], Haoran Qu[a], Jialin Mao[b], Ruobing Bai[a], Shuailin Zhang[a], Xueyan Feng[a], Chrys Wesdemiotis[a,b], Xue-Hui Dong[c,d,e,**], Stephen Z.D. Cheng[a,c,d,*]

[a] Department of Polymer Science, The University of Akron, Akron, OH, 44325, USA
[b] Department of Chemistry, The University of Akron, Akron, OH, 44325, USA
[c] South China Advanced Institute of Soft Matter Science and Technology, South China University of Technology, Guangzhou, 510641, China
[d] International School of Molecular Science and Engineering, Guangzhou International Campus, South China University of Technology, Guangzhou, 510641, China
[e] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China

## HIGHLIGHTS

- Iterative method is a powerful way to synthesize macromolecules with precise structures.
- The shapes of linkers have great impact on the nano-structures formed.
- The rigidity of the hydrophobic part is the key of nano-structure transformation.

## ARTICLE INFO

*Keywords:*
Linker effect
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## ABSTRACT

In this work, we studied the linker effect on the nanostructures of a serious of specifically designed, functionalized polyhedral oligomeric silsesquioxane (POSS) based Dendron-like macro-isomers. The varying linkers between hydrophilic and hydrophobic POSS cages lead to topological isomers with identical composition but different molecular shapes. Their unique phase behaviors highlight remarkable effects of molecular architectures on the formation of nanostructures. Due to topological constraints, these macro-isomers assume either a fan- or a cone-molecular shape, which assembles into either hexagonally packed cylindrical phase (HEX) or Frank-Kasper A15 phase. This work provides guiding rules on designing precise molecular nanostructures with desired properties *via* linker engineering.

## 1. Introduction

Molecular topologies can significantly affect thermal, rheological, mechanical, and other properties of materials [1–5]. For example, the cyclic polymers exhibit higher glass transition temperatures ($T_g$), smaller hydrodynamic volumes, as well as lower degree of entanglement, as compared with their linear counterparts [6,7]. In addition, topological differences also have great influence on the nano-structures formed [3–5]. Previously, systematic studies have been conducted on $AB_n$ type dendrons with a hydroxyl-functionalized polyhedral oligomeric silsesquioxane (DPOSS) connecting to different numbers of isobutyl-functionalized POSS (BPOSS) cages *via* flexible linkers [8]. The number of BPOSS has been systematical varied, while the linkers remain identical. It has been identified that with increasing number of BPOSS, the supramolecular structure evolves from lamellae (Lam), hexagonally packed cylinders (HEX), to Frank-Kasper A15, sigma, and finally to body centered cubic (BCC) structures [8]. The role of the geometry of the linkers on the formation of supramolecular structure, however, is still elusive.

To address this question, we design a series of dendrons with identical composition while the linkages are arranged in different geometries, which could be regarded as topological isomers. The

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* Corresponding author. Department of Polymer Science, The University of Akron, Akron, OH, 44325, USA.Department of Polymer Science, The University of Akron, Akron, OH, 44325, USA.

** Corresponding author. South China Advanced Institute of Soft Matter Science and Technology, South China University of Technology, Guangzhou, 510641, China.

*E-mail addresses:* xdong@scut.edu.cn (X.-H. Dong), scheng@uakron.edu (S.Z.D. Cheng).

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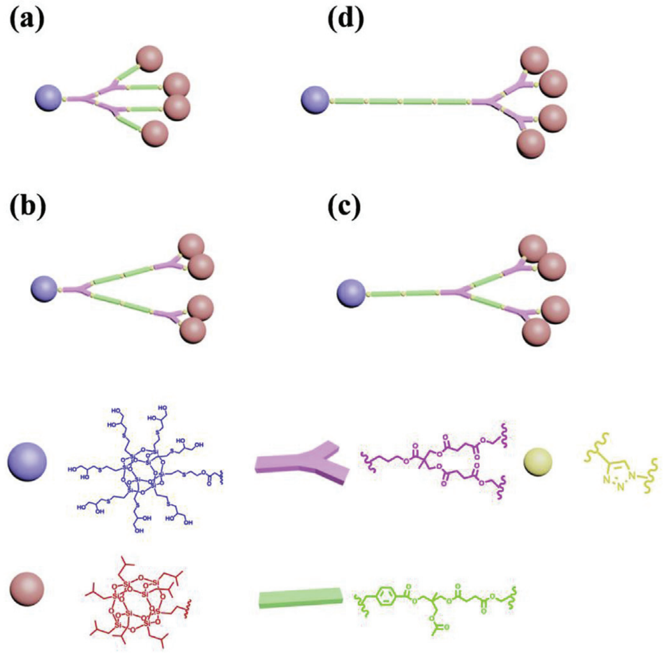


**Fig. 1.** Structure illustration of Macro-isomer **1** (a), Macro-isomer **2** (b), Macro-isomer **3** (c), and Macro-isomer **4** (d). Detailed molecular structures of building blocks are listed below.

dendrons are composed of DPOSS and BPOSS cages which were connected via flexible linkers, as shown in Fig. 1. The molecular structure consists of three parts, DPOSS component at the apex, BPOSS component at the periphery, and a flexible linker in between. These dendrons could serve as a unique model system to elucidate the importance of geometrical constraints imposed by the linkers on the assembled nanostructures.

Iterative divergent convergent method (IDC) is a powerful method in preparation of dendrons with precise molecular weight and specific chemical structures [9–11]. In the case that only one type of monomer is used, either linear homo-polymers or dendrimers would be achieved [13]. In this study, two different monomers, a linear monomer with two reactive sites (Fig. 1 green) and a Y-shape monomer with three reactive sites ((Fig. 1 purple)), are included to diversify the topologies of the linker. Four dendrons with the same molecular weight but different topologies are designed and synthesized accordingly (Fig. 1). Hydrophilic and hydrophobic POSS particles are then attached to the apex and the periphery of the dendritic linker, respectively, resulting in giant topological isomers.

Copper catalyzed azide-alkyne cycloaddition (CuAAC) is well known as a model "click" reaction due to its highly efficient, modular, and robust feature [11,14–16]. It has been widely applied in macromolecular synthesis [17,18]. CuAAC "click" reaction was employed in this study to ensure high yield in each step. Thiol-ene reaction, which is another "click" reaction, was also applied to install hydroxyl group on the apex of all four macro-isomers following the procedure reported before [19]. All the characterization data clearly confirm the structure and purity of both the intermediates and final products. Detailed $^1$H NMR of four isomers and some important intermediate products can be found in Fig. S5. The gel permeation chromatography (GPC) shows mono-dispersed peaks with narrow distribution (Fig. S1). The matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) data exhibit a single peak, and the observed molecular weight and calculated molecular weight are in good agreement, confirming the success of the synthesis (Fig. 2).

These topological isomers were first studied using differential scanning calorimetry (DSC) experiments (Fig. S2). All of them have glass transition temperatures ($T_g$) between 40 and 45 °C which are accredited to the flexible linkers (The flexible linkers possess $T_g$ in the same region, see Fig. S3), while the melting temperatures ($T_m$) lay within the range between 160 and 180 °C, attributing to the melting of BPOSS cages [8].

Small angle X-ray scattering (SAXS) and bright field transmission electron microscopy (TEM) were utilized to investigate the self-assembled structures. All samples were thermally annealed at 200 °C under vacuum for 12 h before quenching to room temperature. The

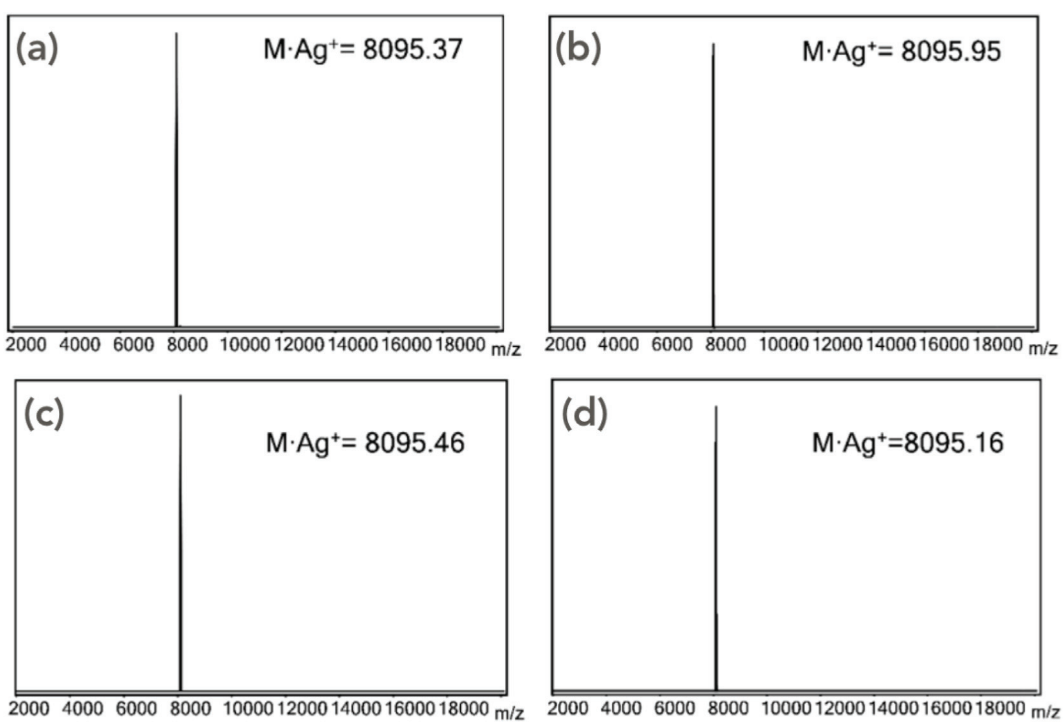


**Fig. 2.** MALDI spectra of Macro-isomer **1** (a), Macro-isomer **2** (b), Macro-isomer **3** (c), and Macro-isomer **4** (d).

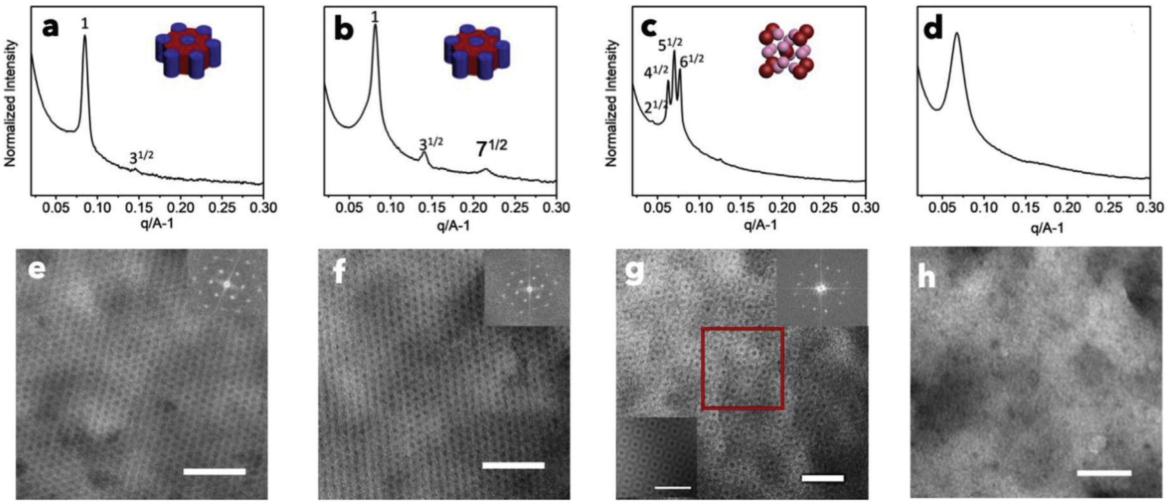


**Fig. 3.** SAXS patterns and bright field TEM images of four macro-isomers: (a, e) Macro-isomer **1**; (b, f) Macro-isomer **2**; (c, g) Macro-isomer **3**; and (d, h) Macro-isomer **4**. Upper right insets are fast Fourier transformation patterns (e, f, g). Lower left inset in Figure g is the corresponding TEM image after Fourier filter. TEM specimens were stained with $OsO_4$. The scale bar is 50 nm.

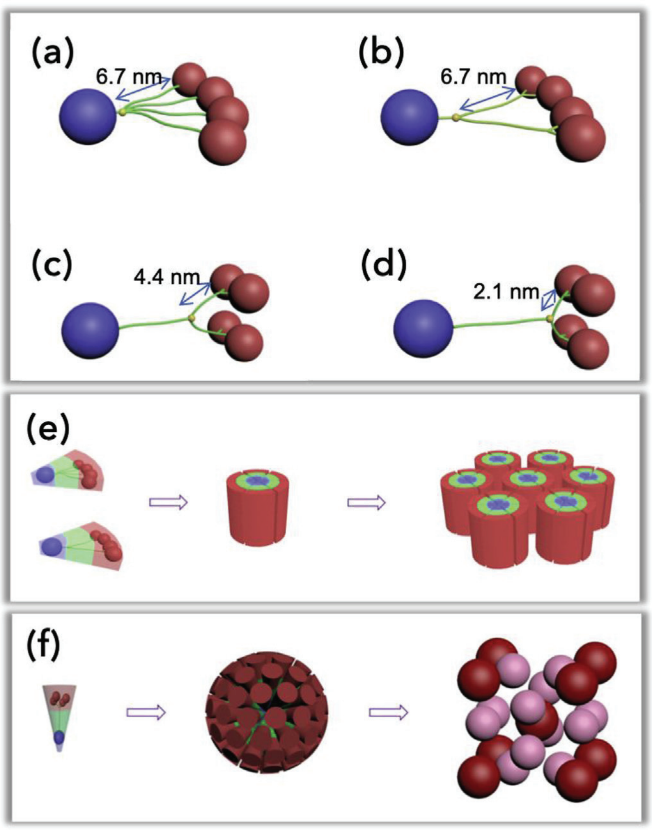


**Fig. 4.** Molecular shapes of Macro-isomer **1** (a), **B** (b), **C** (c), and **D** (d). Fan-shaped molecule and cone-shaped molecule self-assemble into hexagonal packing (e) and A15 packing (f), respectively.

SAXS pattern of Macro-isomer **1** shows diffraction peaks with a $q$-ratio of 1: $\sqrt{3}$ (Fig. 3a), indicating a hexagonal packing structure (HEX), which was further proved by the bright field TEM images as shown in Fig. 3e. The inserted diffraction pattern generated *via* fast Fourier transformation indicates a [000l] zone HEX reciprocal lattice. This HEX lattice possesses a lattice parameter of $a$ = 7.4 nm. Similar to Macro-isomer **1**, Macro-isomer 2 also self-assembles into a HEX structure with $a$ = 7.8 nm, as evidenced by the SAXS pattern (Fig. 3b) and TEM image (Fig. 3f). For Macro-isomer **3**, SAXS pattern shows a set of diffraction peaks in a $q$-ratio of $\sqrt{2}:\sqrt{4}:\sqrt{5}:\sqrt{6}$, which is a typical Frank-Kasper A15 phase with structural parameter of $a$ = 20.2 nm (Fig. 3c) [20]. Fig. 2g is the bright field TEM image of a two-dimensional A15 pattern along the [001] direction. The tiling number of $4^4$ is clearly observed. Interestingly, only one broad peak appears in the SAXS pattern for Macro-isomer **4** (Fig. 3d), indicating no ordered structure exist.

It is evident that the flexible linkers have tremendous effect on the self-assembled structures of the giant molecules, although it is believed that the incompatibility between hydrophobic BPOSS and hydrophilic DPOSS drives phase formation. An immediate question is: where is the location of the linker between DPOSS and BPOSS? A similar $T_g$ was observed in these giant molecules as compared with the linkers themselves, indicating they form a separated domain between DPOSS domain and BPOSS domain (Fig. S3). Combining the molecular geometry and the thermal behaviors, it is reasonable to propose that DPOSS forms the inner core and BPOSSs form the outside shell, with linkers filling up the empty space between them (Fig. 4).

Different from the traditional diblock copolymers in which molecular shape is not a significant factor due to the flexible nature [21], the deformability of hydrophobic domain in this study is the key to the final nanostructures. The arrangement of BPOSS dictates the shape of the hydrophobic domain. In the case of Macro-isomer **1** and **2** (Fig. 4A and B), the junction point (golden sphere) is close to the hydrophilic DPOSS (core), and BPOSSs are attached to this junction point via four individual arms (Macro-isomer **1**) or two individual arms (Macro-isomer **2**). The distance between junction point and BPOSS in Macro-isomer **1** and **2** is 6.7 nm, assuming the linker between them is fully stretched (see equation S(6)). The relative longer spacers provide a larger room for possible packing of BPOSS, and the phase structures are dominated by the composition. The volume fraction of the hydrophobic part of Macro-isomer **1** and **2** is 84.5% (see equation S(5)). From previous report on the self-assembly structures of DPOSS-polystyrene giant molecules, HEX structure was found with volume fraction of hydrophobic part between 80% and 90% [19]. The phase structure formed here is in good accordance with that in the DPOSS tethered with one PS tail system considering the volume fraction of hydrophobic part.

When the junction point is closer to the hydrophobic BPOSSs (periphery), those four BPOSS cages are firmly connected with each other. In the case for Macro-isomer **3** and **4**, the distance between junction point and BPOSS is 4.4 nm (Macro-isomer **3**) and 2.1 nm (Macro-isomer **4**) assuming extended conformation. The constraint between BPOSSs forces BPOSSs packing into two-layer geometry otherwise the linkers would be over-stretched (Fig. 4C and D), and the molecule assume a cone-shape conformation due to the mismatch of cross section area. These cone-shape molecules pack into sphere first and further assemble into ordered Frank-Kasper A15 structure (Macro-isomer **3**). To keep fan- or cone-shape conformation, some specific conformations should be taken by the linkers to fill up the free space between DPOSS and BPOSS cages. This requires the linker to be flexible enough to take selective conformations, which isn't energetically favored due to the semi-rigid nature of the linker in Macro-isomer **4**.

In this work, four topological macromolecular isomers were specifically designed and synthesized. A variety of nanostructures were observed simply by tuning the architecture of the linker, which arranges POSS cages into different geometries. The phase structure evolution suggests that the freedom of the hydrophobic BPOSS, determined by connection sequence among molecules, have great impact on the nanostructures. The phase structures are primarily dictated by volume fraction if the linker is flexible enough. Once the hydrophobic domain become less deformable, unconventional nanostructures including A15 phase appear. This study provides possibilities of fine-tuning self-assembly structures through molecular topological effect.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2019.01.051.

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