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Mixed star-shaped POSS-based molecule with hydroxy group-containing units and azobenzene fragments as two types of arms

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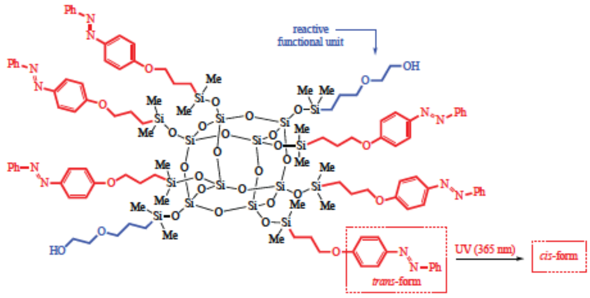
Novel branched organic–inorganic nanoparticles with cubic octahedral silsesquioxane core containing the statistically grafted photoactive azobenzene fragments and 2-hydroxyethyl groups were synthesized *via* hydrosilylation coupling. Preservation of the photochromic properties of the reactants in the final product was revealed.



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Silica-based compounds, in particular polyhedral oligomeric silsesquioxanes (POSS), are the representative building blocks for hybrid materials with superior properties.[1–5] The cubic T8-POSS scaffold with eight variable functional groups is one of the best studied types of POSS conjugates. The covalent attachment of organic components to such T8-POSS core results in highly branched star-like systems.[6,7] For example, upon attaching azobenzene arms, the light-responsive star-shaped azo-POSS nanostructures with suppressed crystallization and stacking ability as well as high thermal stability and nanocomposite film-forming ability have been obtained.[7–10] However, most of the works in the field of functionalized polyoctahedral silsesquioxanes focus on POSS-based compounds with uniform arm composition.

Currently there is an intense interest in the synthesis of POSS derivatives with different types of substituents on the Si atom at the vertex of the T8 cage (typically so-called bifunctional POSS).[11–18] This approach enables the synthesis of linear polymers with T8-unit in their backbone, and such polymers have a broader spectrum of properties and areas of their application.[16–18] Furthermore, POSS nano-building blocks with two types of functional moieties/groups on the T8-POSS core are effective precursors for the preparation of self-assembled star-shaped Janus molecules.[11–15] Thus, mixed [2 : 6], [3 : 5] and [4 : 4] hetero-arm star structures based on Janus POSS have been synthesized in recent years. These systems were mainly obtained from the initial octafunctionalized POSS with hydroxy group-containing units as one of the two functional fragments. Notably, the hydroxy groups are suitable for various modifications thus providing a broad range of polymers.

To the best of our knowledge, combination of hydroxy groups (as the first functionality) and azobenzene fragments (as the second functionality) in the POSS structure has not been reported yet. We believe that synthesis of bifunctional POSS conjugates with photo-switchable azobenzene fragments as one type of functional units may open up new possibilities for fine-tuning the self-assembly of POSS materials and their properties at least through controlling azobenzene configuration. Herein, we synthesized the mixed [2 : 6] star-shaped POSS system composed of two different types of functional units, namely, 2-hydroxyethyl groups and azobenzene fragments.

Octakis(dimethylsilyloxy)silsesquioxane $(HSiMe_2O)_8Si_8O_{12}$, compound **1** (Scheme 1), is one of the most versatile commercially available scaffolds and can be readily functionalized using simple hydrosilylation reaction as a reliable method for the Si–C bond formation.[8–10] Hence, the statistically bifunctional silsesquioxane **4** was synthesized in a one-pot manner by the hydrosilylation reaction between scaffold **1** (1 equiv.) and a mixture of allyl-based azobenzene **2** (6 equiv.) as photoactive unit and 2-allyloxyethanol **3** (2 equiv.).[†] Typically, the protection of hydroxy groups during the hydrosilylation is essential because they can easily react with Si–H bonds (O-silylation).[8] We chose compound **3** for introduction of hydroxy group-containing moieties into POSS **4** since it was shown that direct hydrosilylation of octakis(dimethylsilyloxy)silsesquioxane with unprotected 2-allyloxyethanol gave exclusive C-silylation products.[19] Product **4** was purified by simple filtration through silica followed by re-precipitation. Conjugate **4** appears as a dark orange powder soluble in toluene and chloroform.

Idealized structure for compound **4** (see Scheme 1) comprises substitutions at the opposite vertices of the T8 cage and only mixed [2 : 6] bifunctional POSS. Note that one of the molecular parameters of bifunctional T8-POSS nanoparticle is the distribution of different types of functional arms, including the distribution in 3D space. Basically, the grafting of heteroarms on POSS structure gives statistical mixture of multifunctional cages (structural isomers and stereoisomers) that are difficult to

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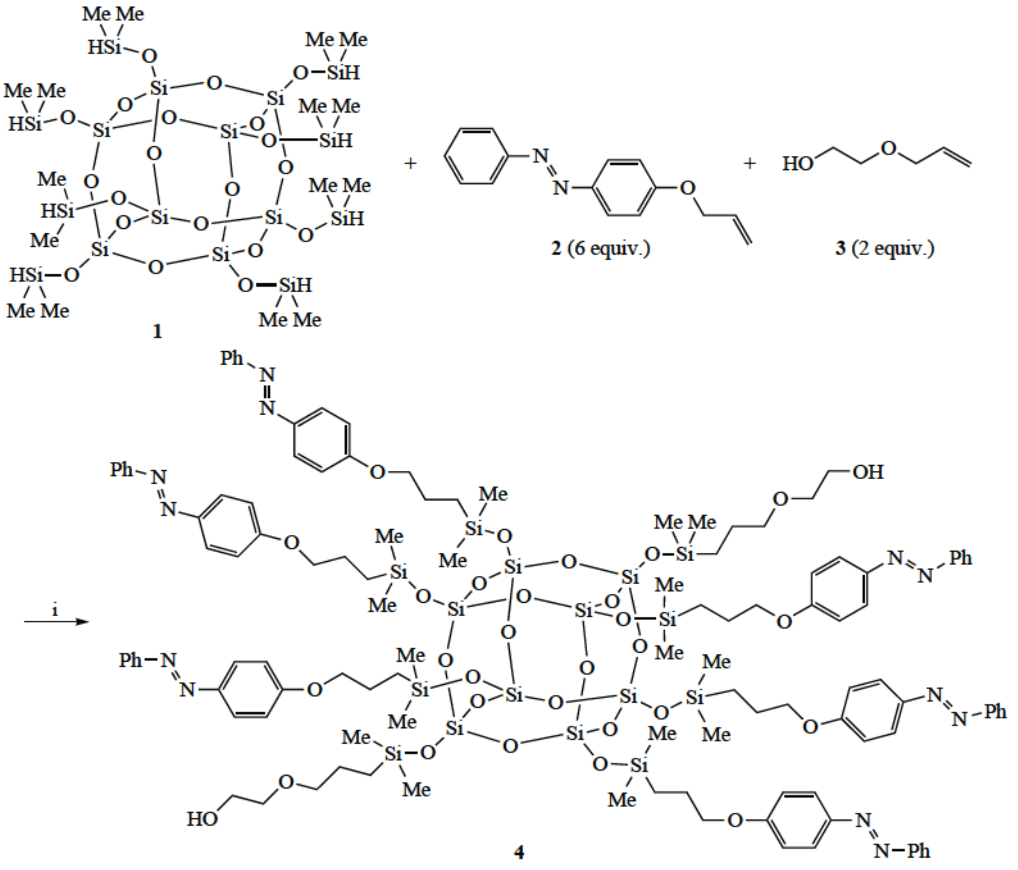
[†] For details, see Online Supplementary Materials.



Scheme 1 *Reagents and conditions*: i, Karstedt's catalyst, toluene, 40 °C, 24 h.

separate.[14] Nevertheless, even bifunctional POSS mixtures with the different statistical distribution of functional branches may show interesting new properties (Janus-like properties as example).[15,20] Importantly, the attachment of functional groups in a statistical manner does not require time-consuming sample preparation or sample handling procedure. Thus, in this study we focus on preparation of azo-based OH-containing POSS conjugate with statistical architectures of its heteroarms.

Application of MALDI-TOF spectrometry has revealed that statistical mixture of POSS **4** mainly contains, as expected, $(RSiMe_2O)_6(R'SiMe_2O)_2Si_8O_{12}$ molecules as well as $(RSiMe_2O)_7(R'SiMe_2O)_1Si_8O_{12}$ derivatives (where R is azobenzene-based fragment and R′ is 2-hydroxyethyl-based units).[†] The formation of branched POSS conjugates such as $(RSiMe_2O)_8Si_8O_{12}$, $(RSiMe_2O)_7(HSiMe_2O)Si_8O_{12}$ and $(RSiMe_2O)_6(R'SiMe_2O)(HSiMe_2O)Si_8O_{12}$ was also detected by MALDI-TOF mass spectrometry with peaks at *m/z* 2924, 2686 and 2550, respectively.

The successful grafting of both azobenzene **2** and compound **3** onto initial POSS scaffold **1** was additionally indicated by FTIR spectrum, which revealed the disappearance of the Si–H characteristic absorption band at 2140 cm^{-1}. ^{1}H and ^{13}C NMR spectroscopy analysis further fully confirmed the formation of bifunctional silsesquioxane with the general formula $(RSiMe_2O)_6(R'SiMe_2O)_2Si_8O_{12}$. Thus, both sets of signals from the propoxy-azobenzene units and propoxy-ethanol-based fragments as well as from POSS core were present in the ^{1}H and ^{13}C NMR spectra of the resulting system **4**. The obtained system **4** has a typical azobenzene absorbance with a strong π–π* band at 348 nm and a weaker n–π* transition at around 440 nm.

Azobenzene-based compounds are known to undergo light-stimulated *trans–cis* photoisomerization when the π–π* transition is excited.[21] Importantly, the branched bifunctional POSS sample **4** synthesized here shows photoisomerization behavior. Figure 1 represents UV-VIS spectra of sample **4** under UV irradiation at 365 nm in chloroform solution.

We found that the photoisomerization reached a photostationary state within 40 s while the first-order rate constant of photoisomerization was 0.1135 s^{-1} (inset of Figure 1). These data are comparable to results of our previous study on the similar azobenzene POSS-based systems[8] and indicate that grafting of hydroxyl-containing units does not prevent photoisomerization reaction to occur. Note that the conjugate **4** has shown a typical reverse isomerization ability induced by irradiation with visible light.

The thermal properties and photoisomerization behavior in ultra-thin nanocomposite film of the obtained compound are now being studied. Next, for comparison, we are going to synthesize mixed [2 : 6] star-shaped POSS-based molecule with

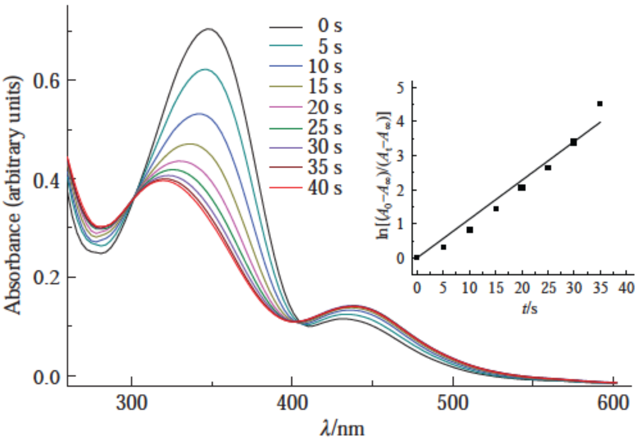


Figure 1 Photoisomerization of substance **4** in $CHCl_3$ solution. Inset shows the first-order plot for *trans–cis* photoisomerization.

precisely defined arms (hydroxy group- and azobenzene-based ones) distribution. It can be achieved using a two-step protocol in which either intermediate $(RSiMe_2O)_6(HSiMe_2O)_2Si_8O_{12}$ or $(HSiMe_2O)_6(R'SiMe_2O)_2Si_8O_{12}$ will be isolated and then reacted with the second functional monomer. It should be noted that hydroxy groups not only represent a versatile function but they could serve as a handle for the purification (for example, using simple chromatography on silica gel) of multifunctional POSS compounds.[11]

In summary, we have reported a facile way to prepare new branched POSS-based system with two mixed [2:6] functionalities: photochemically switchable azobenzene fragments and hydroxyl-containing units. The occurrence of its photoisomerization in solution was confirmed with conventional UV-VIS spectroscopy. The photoresponsive feature of the resulting nanoparticle is an effective instrument for designing a wide range of stimuli-responsive and optical active materials. Hence, the obtained system can be used as nano-building block for the preparation of both molecular and macromolecular systems (Janus star polymers as example) with self-assembled structures and desired functions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.007.

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