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Synthesis and Isolation of Methacrylate- and Acrylate-Functionalized Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12}) and Characterization of the Relationship between Their Chemical Structures and Physical Properties

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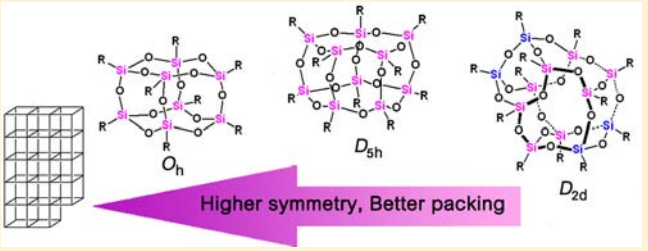
Supporting Information

ABSTRACT: Novel organic−inorganic hybrid nanobuilding blocks of methacrylate- and acrylate-functionalized polyhedral oligomeric silsesquioxanes were easily prepared via nucleophilic substitution on octakis(3-chloropropyl)-octasilsesquioxane, using sodium methacrylate and sodium acrylate, respectively. From a practical standpoint, these cage-rearranged silsesquioxanes (T_8, T_{10}, and T_{12}) could be readily isolated in their pure form with conventional silica gel column chromatography. Octakis(3-propyl methacrylate)-octasilsesquioxane (T_8) is a colorless, crystalline solid with a melting point of 66.7−67.2 °C, while other cage products are colorless viscous liquids at room temperature. Moreover, we report that the chemical structure/physical property relationship of silsesquioxane cages not only is dependent on the symmetry of the inorganic silsesquioxane core at a given temperature but also is dictated by the organic substituent mobility. Structures of the products were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and high resolution electrospray ionization mass spectrometry analysis.



INTRODUCTION

Acrylate and methacrylate esters are reactive unsaturated monomers that form polymers that have numerous applications as adhesives, coatings, photopolymer printing plates, and contact lenses.[1] These monomers can also be utilized for organic synthesis in Michael additions with enolates,[2] amines,[3] and thiols.[4] More recently, significant attention has been placed on organic−inorganic hybrid materials, particularly the polyhedral oligomeric silsesquioxanes. These hybrid molecules generally consist of an inorganic core made up of a Si−O framework, which is covalently surrounded by organic groups, giving them a dendritic-like structure.[5] For example, octakis(3-chloropropyl)octasilsesquioxane, T_8 (**1**),[6] bearing 1° alkyl chlorides, can be readily modified to contain various functional groups (e.g., azide,[7] thioester,[8] cyano,[9] phthalimide,[10] bromo, and iodo[11]) via nucleophilic substitution reactions. Nevertheless, some studies have found that inorganic phase transformation of the T_8 cage into cage-rearranged products (T_8, T_{10}, and T_{12}) is promoted by strong nucleophiles during substitution reactions.[7,10] Recently, polyhedral oligomeric silsesquioxanes have found a use in materials science as nanocomposites,[12] in optoelectronics,[13] and in biotechnology[14] and as catalysts.[15]

In order to broaden the applications of polyhedral oligomeric silesquioxane chemistry, it is necessary to develop new types of reactions. In this study, we report on the design, synthesis and characterization of multimethacrylate and acrylate organic functions for silsesquioxane cage-like structures (T_8, T_{10}, and T_{12}). Here, we performed characterization with the clean and purified forms of these compounds for the first time, in contrast to previous reports, which have only relied on crude mixtures of freshly prepared[16] and commercially available products[17] without further purification. Moreover, several important aspects regarding the optimal reaction conditions were not taken into consideration in those studies. We report several relationships between the chemical structures of each pure silsesquioxane cage and its physical properties. For example, octakis(3-propyl methacrylate)octasilsesquioxane (**2**) is a colorless, crystalline solid, which makes it unique among other silsesquioxanes, which are in the liquid state at room temperature.

RESULTS AND DISCUSSION

Preparation and Characterization of Methacrylate-Functionalized Cage-Rearranged Silsesquioxanes. We first prepared **2**, decakis(3-propyl methacrylate)-decasilsesquioxane (**3**), and dodecakis(3-propyl methacrylate)-dodecasilsesquioxane (**4**) through nucleophilic substitution reactions. Upon treatment of **1** with sodium methacrylate in

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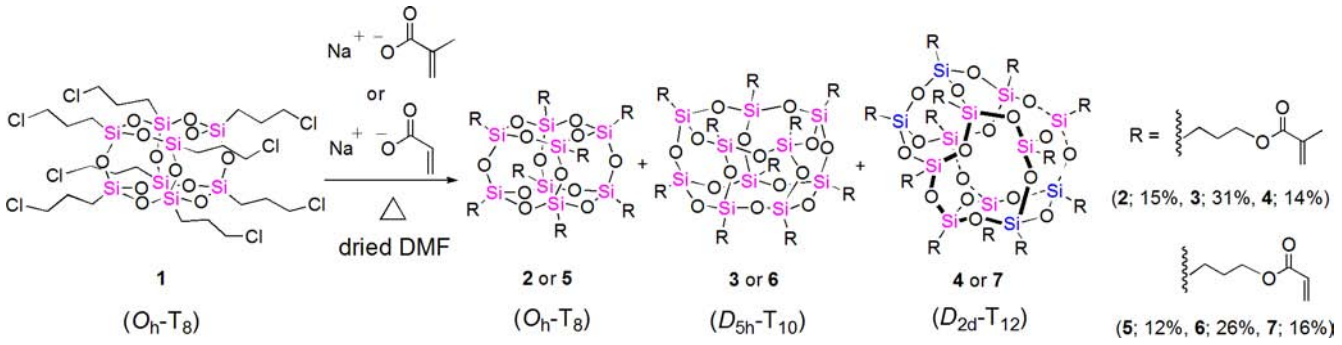
Scheme 1. Cage-Rearranged T_8 of Compound 1 upon Full Introduction of Methacrylate and Acrylate Functions, Leading to (a) Compounds 2−4 (70 °C, 2 days, 0.048 mol L^{-1}, 1.4 equiv of Sodium Methacrylate/$RSiO_{3/2}$) and (b) Compounds 5−7 (100 °C, 1 day, 0.098 mol L^{-1}, 1.4 equiv of Sodium Acrylate/$RSiO_{3/2}$)



anhydrous *N*,*N*-dimethylformamide (DMF) at 70 °C (Scheme 1a), an almost complete substitution conversion (~98%) of the crude product could be observed within 48 h, as monitored by the shift in the ^{1}H NMR peaks from 3.53, 1.82, and 0.75 (3-chloropropyl groups) to 4.09, 1.74, and 0.68 (3-methacryloxypropyl groups) ppm, respectively.

Meanwhile, we observed extensive cage rearrangement (T_8 cage) of **1** through the presence of four very distinguishable singlet signals in the ^{29}Si{^{1}H} NMR spectrum of the crude product (Figure 1) at −66.81, −68.44, −68.68, and −71.14

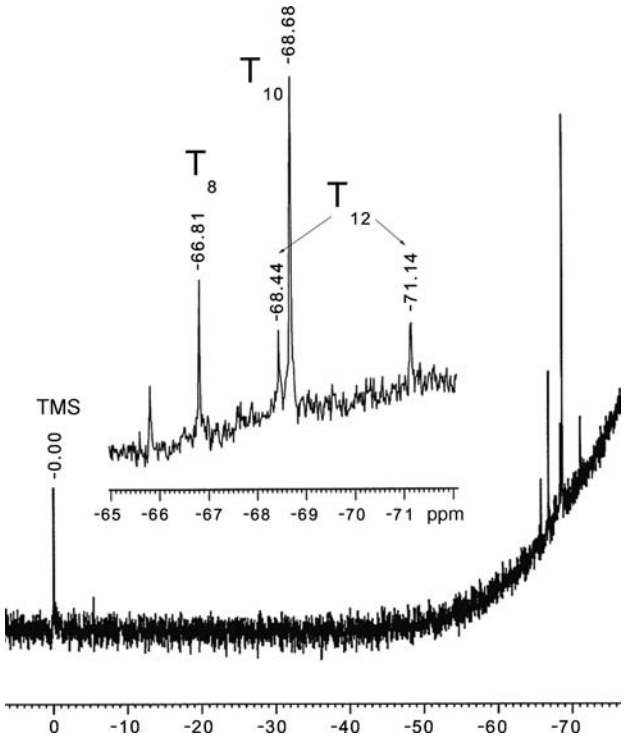


Figure 1. ^{29}Si{^{1}H} NMR spectrum of the crude product of methacrylate-functionalized polyhedral oligomeric silsesquioxanes.

ppm. Unambiguously, this crude product consists of a cage mixture of T_8 (**2**; −66.81 ppm), T_{10} (**3**; −68.68 ppm), and T_{12} (**4**; −68.44 and −71.14 ppm). In addition to undergoing substitution reactions, it is likely that methacrylate anions further attack, cleave, fragment, and reassemble the Si−O−Si bonds of the inorganic core, leading to the formation of a thermodynamically stable mixture of cage-rearranged products (T_8, T_{10}, and T_{12}). This phenomenon is possible due to the direct effects of the electron-withdrawing groups present and the low steric hindrance of the 3-substituted propyl chains on the silsesquioxane cage under these harsher reaction conditions in which there are stronger nucleophiles present.[7a,10,18] According to satisfactory chromatographic analysis on thin-layer chromatography (TLC) plates with silica gel, their isolation to obtain each pure product was carefully examined.

In Figure 2, we found that only by using conventional silica gel column chromatography in a solvent mixture of ethyl acetate/*n*-hexane (3:7), the crude product (0.80 g) could be easily separated into **3** (T_{10}; 0.25 g; R_f = 0.40) as a major product, while **2** (T_8; 0.12 g; R_f = 0.45) and **4** (T_{12}; 0.11 g; R_f = 0.35) are present as minor products. It is worth noting that purification was necessary because we also observed an intense baseline upon TLC separation under UV light. This indicates that during substitution reactions side reactions likely occur, yielding unwanted by-products or polar components of polysilsesquioxanes. Apparently, compound **2** in the T_8 cage is a crystalline solid with a melting point of 66.7−67.2 °C, while the other cages (**3**, T_{10}; **4**, T_{12}) are in the liquid phase (viscous fluidlike substances) at room temperature. These specific physical properties also support our recent observation on the states of matter of cage-rearranged phthalimide-functionalized polyhedral oligomeric silsesquioxanes. Although the colorless crystal of the T_8 cage (mp 247−248 °C), the amorphous-like white-fluffy formation of the T_{10} cage (T_g ~ 65 °C), and the thin film of the T_{12} cage are all solids at room temperature, the symmetry could be a key to determining the relative lattice energies because higher symmetry allows for better packing and higher phase-transition temperatures in the solid state.[10] In polyhedral geometry, the higher degree of symmetrical faces in a cage is typically thought to allow neighboring molecules to get very close in three-dimensional space.

All faces in a T_8 cube (O_h) mainly consist of six symmetrical 8-membered rings of an inorganic Si−O−Si core, in contrast to lower-symmetrical cages like T_{10} (D_{5h}; five 8-membered and two 10-membered rings) and T_{12} (D_{2d}; four 8-membered and four 10-membered rings). Therefore, close-packed and crystallized states are usually observed in the T_8 cage.[8,10,11] In addition, the flexible Si−O−Si bond makes the larger cages change shape easily, also contributing to the low crystallinity of these compounds. We suggest that the tendency to form such a condensed matter for these compounds would be T_8 > T_{10} > T_{12}.

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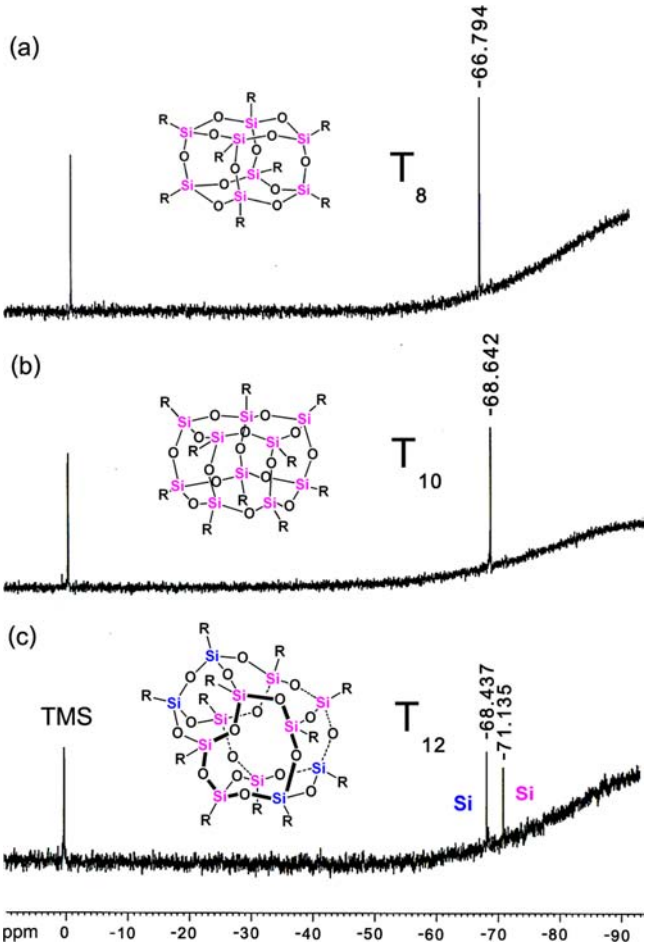

Figure 2. $^{29}Si\{^{1}H\}$ NMR spectra of purified compounds (a) octa-, (b) deca-, and (c) dodecameric methacrylate-functionalized silsesquioxanes (**2**–**4**).

Preparation and Characterization of Acrylate-Functionalized Cage-Rearranged Silsesquioxanes. In order to prepare octakis(3-propyl acrylate)octasilsesquioxane (**5**), decakis(3-propyl acrylate)decasilsesquioxane (**6**), and dodecakis(3-propyl acrylate)dodecasilsesquioxane (**7**), the reaction conditions between **1** and acrylate anion were also studied. As expected, the substitution rate on **1** at 70 °C with an acrylate anion was slower than that with methacrylate anions, and the substitution conversion after 2 days reached only 55%. We suggest that the difference in the relative nucleophilicity between methacrylate and acrylate anions is due to the differences in the electron density on the nucleophilic oxygen. In fact, acrylic acid has a higher K_a value, and thus the acrylate anion could be considered to be more stable or less reactive than the methacrylate anion.[19] As the temperature increased up to 100 °C, the substitution reaction with an acrylate anion was found to be almost complete (~96%) within 24 h (Scheme 1b). Similarly, the pattern of the $^{29}Si\{^{1}H\}$ NMR spectrum of the crude product also reveals the existence of a cage mixture of T_8 (**5**; −66.81 ppm), T_{10} (**6**; −68.69 ppm), and T_{12} (**7**; −68.47 and −71.18 ppm). We hypothesize that the acrylate anion plays the same role as the methacrylate anion in the induction of cage rearrangement of the silsesquioxane. After 0.90 g of crude mixture was passed through a silica column chromatography (ethyl acetate/*n*-hexane: 2:3), compounds **5** (T_8; 0.11 g; R_f = 0.40), **6** (T_{10}; 0.23 g; R_f = 0.35), and **7** (T_{12}; 0.14 g; R_f = 0.25) were successfully isolated in their pure forms. However, all three cages found in viscous liquids are similar to the case of cage-rearranged azido-functionalized polyhedral oligomeric silsesquioxanes.[7a]

To understand the effects of relative organic substituents on some physical properties, it was known that poly(methyl acrylate) is a soft rubber but poly(methyl methacrylate) is a strong, hard, and clear plastic at room temperature.[1] Thus, only a small methyl group is able to have a significant impact on the physical properties and behavior of the material. As it turns out, how soft or hard a silsesquioxane cage is not only is dependent on the identity of the inorganic core at a given temperature but also is determined by organic substituent mobility, or how easily the substituents move and pass around each other. If the organic substituents between molecules can glide smoothly over each other, the overall whole mass of molecules will be able to flow more easily. Thus, a silsesquioxane cage, which has lower substituent mobility, will be more rigid and have lower flexibility, whereas one that has higher substituent mobility will be softer and more pliable.

CONCLUSION

Octa-, deca-, and dodecameric methacrylate- and acrylate-functionalized silsesquioxanes were successfully synthesized and readily isolated in their pure forms through conventional column chromatography. Organic−inorganic silsesquioxane domain-based features allow us to understand the chemical structure−physical property relationships. Rather than using a mixture, the authors believe that using such an application for each pure silsesquioxane monomer could diversely obtain the specific properties of a material.

EXPERIMENTAL SECTION

Materials. (3-Chloropropyl)trimethoxysilane (purity >95.0%) was purchased from Tokyo Chemical Industry Co., Ltd., and used without additional purification. Sodium methacrylate (purity >99.0%), sodium acrylate (purity >97.0%), and anhydrous *N*,*N*-dimethylformamide (DMF) were purchased from Sigma Aldrich, while commercial-grade ethyl acetate and methylene chloride were further distilled. Precoated silica gel 60 F_{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck & Co., Inc.

Physical Measurement and Instrumentation. Fourier transform NMR spectra were obtained using a Bruker-DPX 300 high-resolution NMR spectrometer for ^{1}H nuclei (300 MHz), a Bruker's Ascend 400 high-resolution magnetic resonance spectrometer for ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (100 MHz), and $^{29}Si\{^{1}H\}$ (79 MHz) nuclei, and a Bruker-AV 500 high-resolution magnetic resonance spectrometer for ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (125 MHz), and $^{29}Si\{^{1}H\}$ (99 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane (TMS), and residual solvent peaks were used as a reference. High-resolution mass spectrometry (HRMS) was performed with a VQ-TOF 2 Micromass spectrometer. Melting points were obtained using a Gallenkamp Sanyo melting detector.

Synthesis of Methacrylate-Functionalized Cage-Rearranged Silsesquioxanes. *Octakis(3-propyl methacrylate)-octasilsesquioxane (**2**), Decakis(3-propyl methacrylate)-decasilsesquioxane (**3**), and Dodecakis(3-propyl methacrylate)-dodecasilsesquioxane (**4**).* The starting material consisting of octakis(3-chloropropyl)octasilsesquioxane (**1**) (0.9995 g, 0.964 mmol) freshly prepared according to a previously published procedure[6] and sodium methacrylate (1.1146 g, 10.31 mmol) were added into a two-neck, round-bottomed flask equipped with a condenser and a magnetic stirbar. The mixture was dried under vacuum for 1 h before anhydrous DMF (20 mL) was added. After that, the reaction mixture was heated to 70 °C for 2 days under dry nitrogen. For the workup, deionized ice−water was added into the

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reaction mixture to remove the NaCl byproduct. The solution mixture was then extracted using CH_2Cl_2 (60 mL × 3). The organic phase was collected and extracted further using H_2O (200 mL × 3). The purified organic phase was then dried using anhydrous sodium sulfate, and evaporation of the solvent resulted in a pale-yellow viscous liquid (1.16 g) as the crude product. Subsequently, 0.80 g of the crude product was separated by silica gel column chromatography in a solvent mixture of ethyl acetate/*n*-hexane (3:7) to give compound **2** (0.12 g, 0.084 mmol, 15% yield as a colorless crystal): R_f = 0.45; mp 66.7−67.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 0.70 (t, ^3J(H,H) = 8.30 Hz, 16H), 1.78 (quintet, ^3J(H,H) = 7.49 Hz, 16H), 1.92 (s, 24H), 4.09 (t, ^3J(H,H) = 6.71 Hz, 16H), 5.53 (s, 8H), 6.08 (s, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.06, 18.30, 22.15, 66.30, 125.28, 136.39, 167.35 ppm; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −66.79. HRMS (ESI). Calcd for $C_{56}H_{88}O_{28}Si_8$ + Na^+: *m*/*z* 1456.95 [M + Na^+]. Found: *m*/*z* 1456.3872. Compound **3** (0.25 g, 0.14 mmol, 31% yield as a colorless viscous liquid): R_f = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.68 (t, ^3J(H,H) = 8.24 Hz, 20H), 1.74 (quintet, ^3J(H,H) = 7.38 Hz, 20H), 1.92 (s, 30H), 4.08 (t, ^3J(H,H) = 6.60 Hz, 20H), 5.53 (s, 10H), 6.07 (s, 10H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 8.45, 18.07, 22.14, 66.09, 125.02, 136.23, 167.06; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.64. HRMS (ESI). Calcd for $C_{70}H_{110}O_{35}Si_{10}$ + Na^+: *m*/*z* 1813.44 [M + Na^+]. Found: *m*/*z* 1813.5090. Compound **4** (0.11 g, 0.051 mmol, 14% yield as colorless liquid): R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.68 (m, 24H), 1.75 (m, 24H), 1.92 (s, 36H), 4.09 (m, 24H), 5.53 (s, 12H), 6.08 (s, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.67, 9.21, 18.30, 22.37, 22.48, 66.38, 125.31, 136.38, 167.29; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.44, −71.14. HRMS (ESI). Calcd for $C_{84}H_{132}O_{42}Si_{12}$ + Na^+: *m*/*z* 2173.94 [M + Na^+]. Found: *m*/*z* 2173.6221. Note that repeated chromatography may be required in order to obtain more purified compounds.

Synthesis of Acrylate-Functionalized Cage-Rearranged Silsesquioxanes. *Octakis(3-propyl acrylate)octasilsesquioxane (**5**), Decakis(3-propyl acrylate)decasilsesquioxane (**6**), and Dodecakis(3-propyl acrylate)dodecasilsesquioxane (**7**).* Starting material **1** (1.0205 g, 0.98 mmol) and sodium acrylate (1.0397 g, 11.06 mmol) were added into a two-neck, round-bottomed flask equipped with a condenser and a magnetic stirbar. The mixture was dried under vacuum for 1 h before anhydrous DMF (10 mL) was added. The reaction mixture was then heated to 100 °C for 1 day under dry nitrogen. The workup procedure was the same as that for the synthesis of compounds **2**−**4** and yielded the crude product, a yellow viscous liquid (1.20 g). Subsequently, 0.90 g of the crude product was separated by silica gel column chromatography in a solvent mixture of ethyl acetate/*n*-hexane (2:3) to give compound **5** (0.11 g, 0.083 mmol, 12% yield as a colorless viscous liquid): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.69 (t, ^3J(H,H) = 8.40 Hz, 16H), 1.75 (quintet, ^3J(H,H) = 7.60 Hz, 16H), 4.11 (t, ^3J(H,H) = 6.8 Hz, 16H), 5.80 (d, ^3J(H,H) = 10.4 Hz, 8H), 6.11 (dd, ^3J(H,H) = 10.4 and 17.2 Hz, 8H), 6.39 (d, ^3J(H,H) = 17.2 Hz, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.04, 22.14, 66.14, 128.52, 130.55, 166.13; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −66.81. HRMS (ESI). Calcd for $C_{48}H_{72}O_{28}Si_8$ + Na^+: *m*/*z* 1343.23 [M + Na^+]. Found: *m*/*z* 1343.2836. Compound **6** (0.23 g, 0.13 mmol, 26% yield as colorless viscous liquid): R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.67 (t, ^3J(H,H) = 8.4 Hz, 20H), 1.73 (quintet, ^3J(H,H) = 7.40 Hz, 20H), 4.10 (t, ^3J(H,H) = 6.80 Hz, 20H), 5.79 (d, ^3J(H,H) = 10.4 Hz, 10H), 6.10 (dd, ^3J(H,H) = 10.40 and 17.40 Hz, 10H), 6.38 (d, ^3J(H,H) = 17.40 Hz, 10H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.57, 22.27, 66.15, 128.45, 130.63, 166.10; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.695. HRMS (ESI). Calcd for $C_{61}H_{92}O_{35}Si_{10}$ + Na^+: *m*/*z* 1675.18 [M + Na^+]. Found: *m*/*z* 1675.3585. Compound **7** (0.14 g, 0.07 mmol, 16% as colorless viscous liquid): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.67 (m, 24H), 1.73 (m, 24H), 4.10 (m, 24H), 5.80 (d, ^3J(H,H) = 10.30 Hz, 12H), 6.10 (dd, ^3J(H,H) = 10.71 and 17.3 Hz, 12H), 6.39 (d, ^3J(H,H) = 17.32 Hz, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.60, 9.14, 22.33, 22.45, 66.22, 128.46, 130.62, 166.08; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.47, −71.18. HRMS (ESI). Calcd for $C_{72}H_{108}O_{42}Si_{12}$ + Na^+: *m*/*z* 2005.62 [M + Na^+]. Found: *m*/*z* 2005.4373. Note that repeated chromatography may be required in order to obtain more purified compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, ^{29}Si NMR and ESI-MS spectra giving characterization data for new compounds **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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