Supporting Information

Sequential "Click" Approach to Polyhedral Oligomeric Silsesquioxane-Based Shape Amphiphiles

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Experimental Section

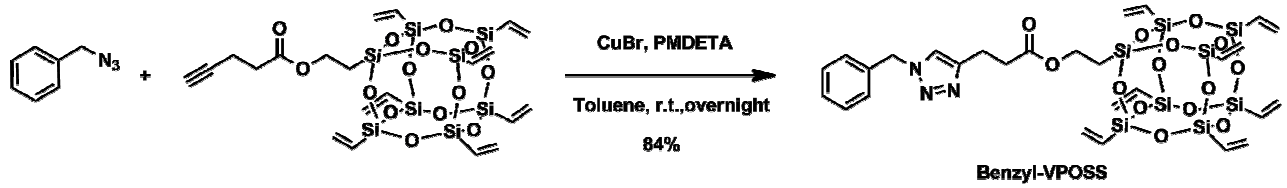
Chemicals. Benzyl bromide (98%, Sigma-Aldrich) was used as received. Benzyl azide was synthesized according to previous literature.[S1]

Benzyl-VPOSS. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added VPOSS-alkyne (100 mg, 0.13 mmol, 1.0 eq.), benzyl azide (17.4 mg, 0.13 mmol, 1.0 eq.), CuBr (1 mg, 0.007 mmol, 0.05 eq.), and freshly distilled toluene (10 mL). The resulting solution was degassed by three freeze-pump-thaw cycles before adding PMDETA (20 mg, 24.1 μL, 1.0 eq.) via pipette. The mixture was further degassed by one cycle, and was then stirred at room temperature for overnight. After the reaction was completed, the solution was directly transferred onto a silica gel column. Toluene was first used as the eluent to fully remove any unreacted starting materials, then a mixture of toluene and ethyl acetate (v/v = 1/1) was used to wash the product off the column. After removal of the solvent, the product Benzyl-VPOSS was obtained as a white powder (98 mg). Yield: 84%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.37 - 7.24 (m, 6H, aromatic protons of the phenyl ring and the triazole ring), 6.13 - 5.88 (m, 21H, vinyl groups), 5.48 (s, 1H), 4.20 (t, J = 5.0 Hz, 2H), 3.01 (m, 2H), 2.69 (m, 2H), 1.16 (t, J = 5.0 Hz, 2H) (Figure S6). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 172.6, 137.1, 137.0, 137.0, 134.8, 129.1, 128.7, 128.6, 128.5, 128.5, 128.0, 60.7, 54.1, 33.6, 29.7, 21.1, 13.1 (Figure S7). MS (MALDI-TOF, *m/z*): calcd. mono-isotopic mass for $[M{\cdot}H]^+$ ($C_{28}H_{38}N_3O_{14}Si_8$): 864.1 Da, found: 864.1 Da; calcd. mono-isotopic mass for $[M{\cdot}Na]^+$ ($C_{28}H_{37}N_3NaO_{14}Si_8$): 886.0 Da, found: 886.1 Da (Figure S8).

Results and Discussion

The reaction between VPOSS-alkyne and benzyl azide was performed to obtain a model compound of VPOSS-PS to investigate the chemical shift of the triazole hydrogen in the ^{1}H NMR spectrum. The reaction followed the procedure to synthesize VPOSS-PS and the product was purified by flash column chromatography. The product Benzyl-VPOSS was obtained as a white powder in a good yield (~84%), and was analyzed by NMR and MS spectrometry. As shown in Figure S6 - S8, the structure of Benzyl-VPOSS

can be unequivocally confirmed. However, as shown in Figure S6, in the ^{1}H NMR spectrum, the resonance signal from the proton on the triazole ring again does not appear clearly as a singlet peak. From the integration of the peaks, it is speculated that this peak appears below 7.50 ppm and is overlapping with those from the benzyl ring protons, which is in contrast to that in VPOSS-PEO (See Figure 5). Nevertheless, the success of the "click" reaction and the precisely defined structure of both Benzyl-VPOSS and XPOSS-PS series can be validated from the combination of other techniques.



Scheme S1. The model reaction between VPOSS-alkyne and benzyl azide to afford Benzyl-VPOSS.

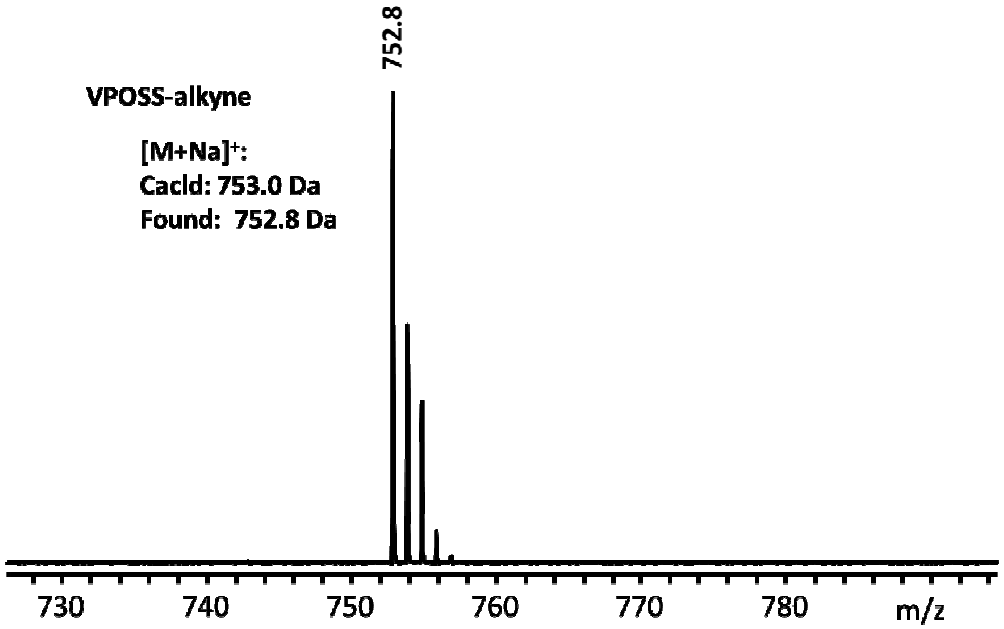


Figure S1. MALDI-TOF mass spectrum of VPOSS-alkyne.

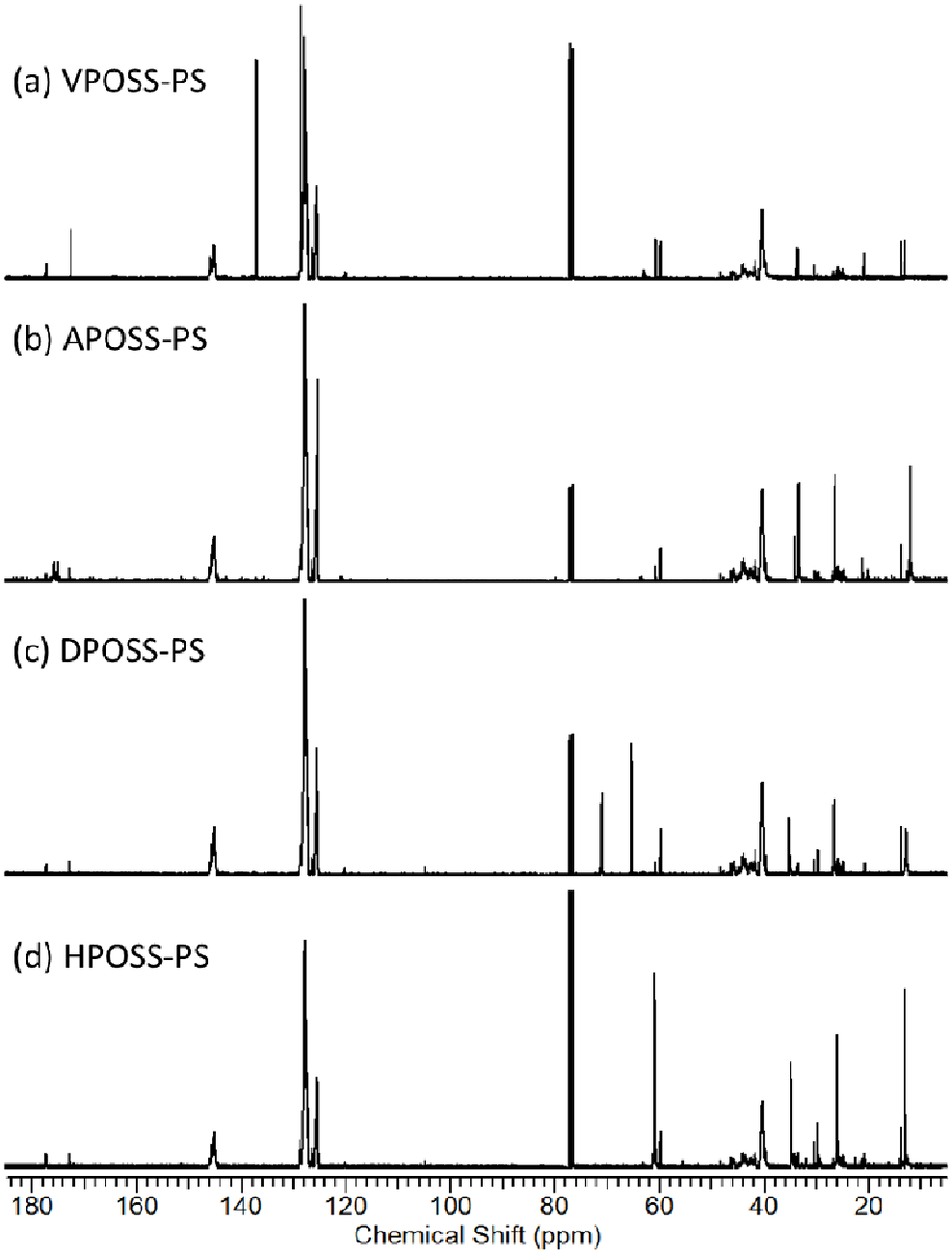


Figure S2. ^{13}C NMR spectra of (a) VPOSS-PS, (b) APOSS-PS, (c) DPOSS-PS, and (d) HPOSS-PS.

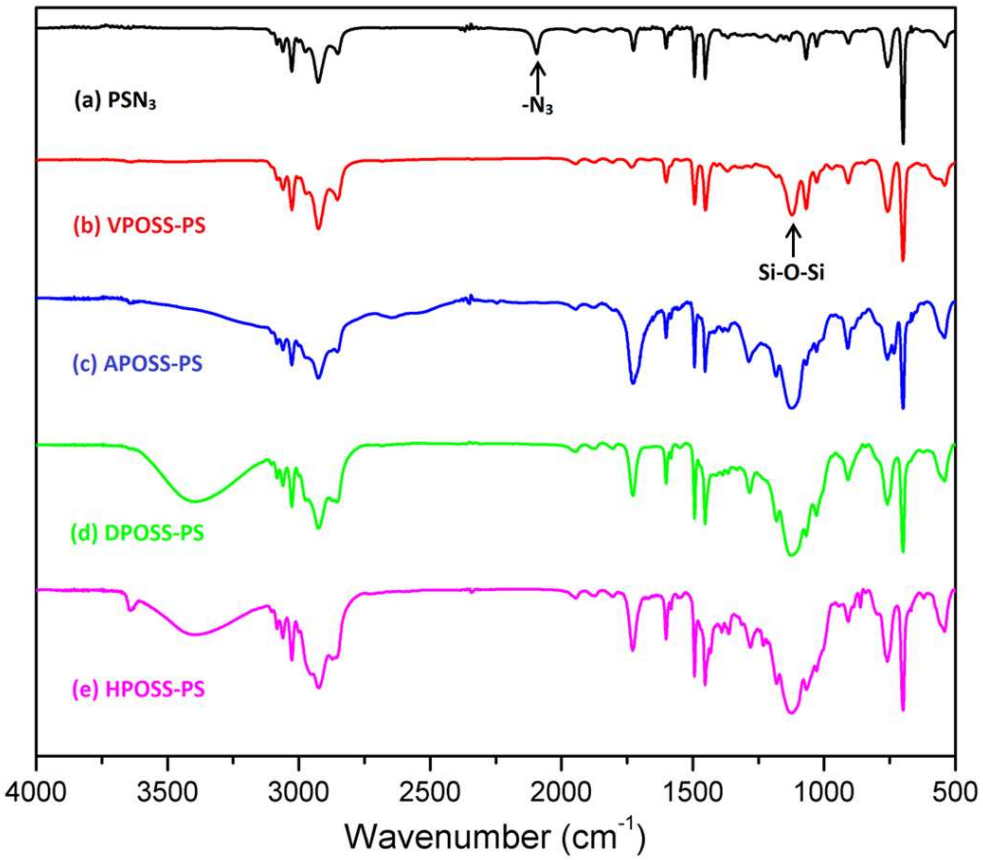


Figure S3. FT-IR spectra of (a) PS-N_3 (black curve), (b) VPOSS-PS (red curve), (c) APOSS-PS (blue curve), (d) DPOSS-PS (green curve), and (e) HPOSS-PS (pink curve).

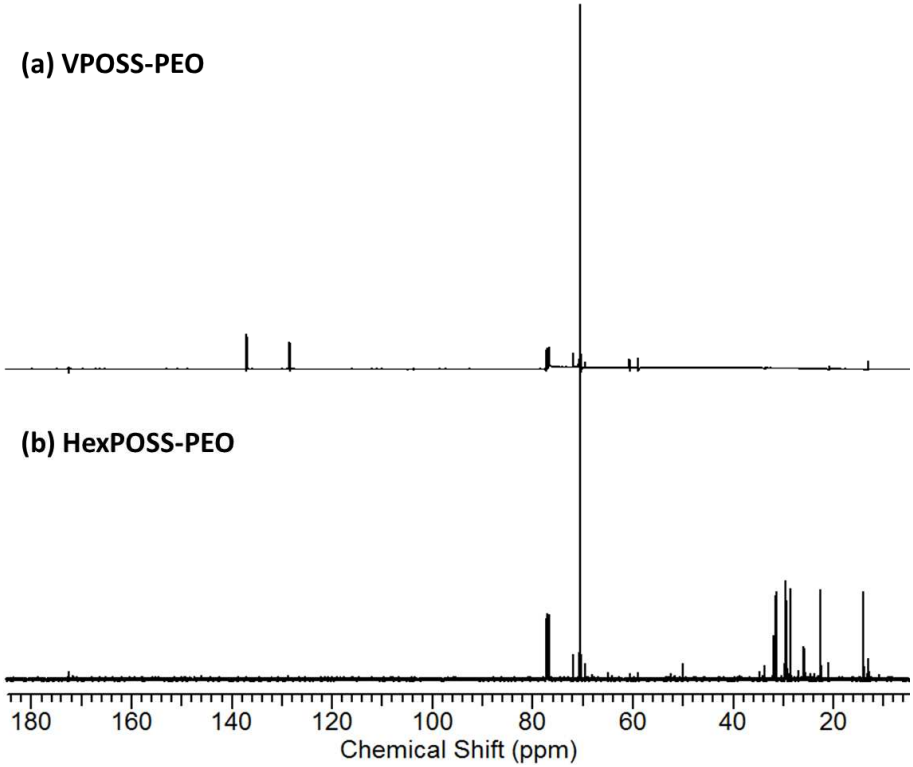


Figure S4. ^{13}C NMR spectra of (a) VPOSS-PEO, and (b) HexPOSS-PEO.

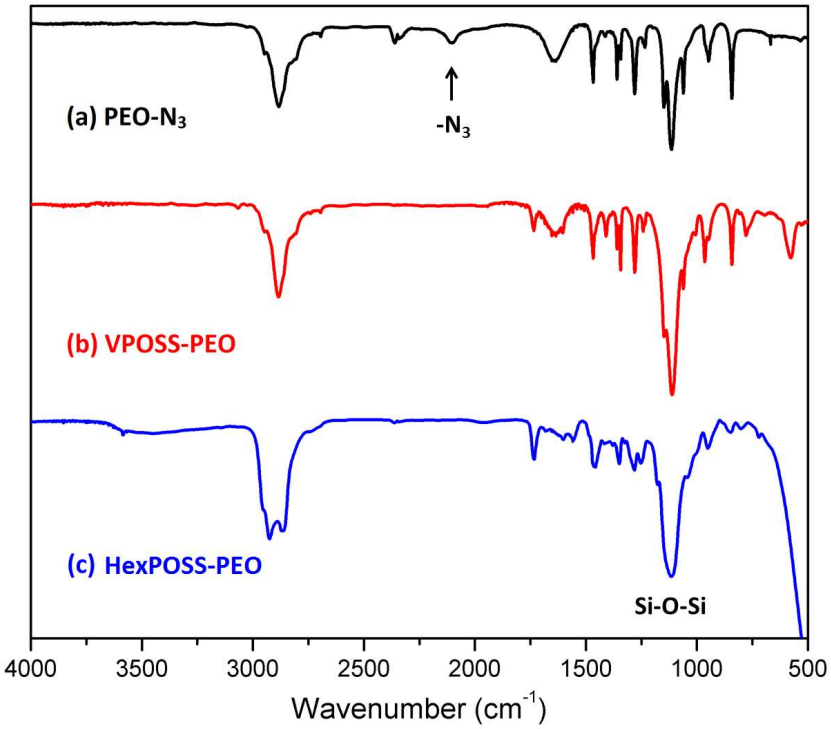


Figure S5. FT-IR spectra of (a) PEO-N_3 (black curve), (b) VPOSS-PEO (red curve), and (c) HexPOSS-PEO (blue curve).

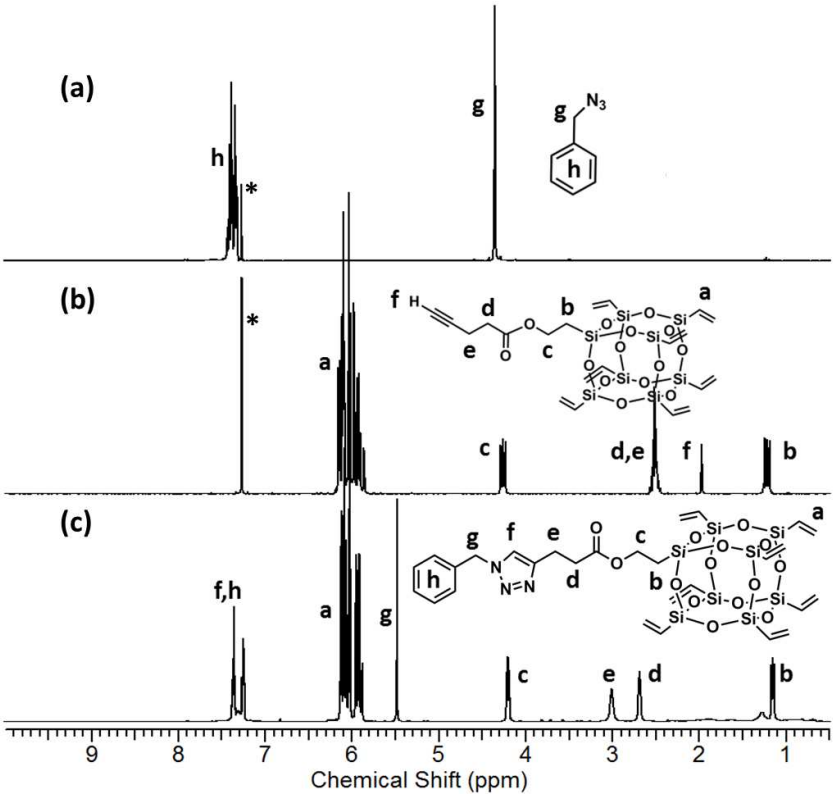


Figure S6. ^{1}H NMR spectra of (a) benzyl azide, (b) VPOSS-alkyne, and (c) Benzyl-VPOSS. The asterisk denotes the resonance peak from residual $CHCl_3$.

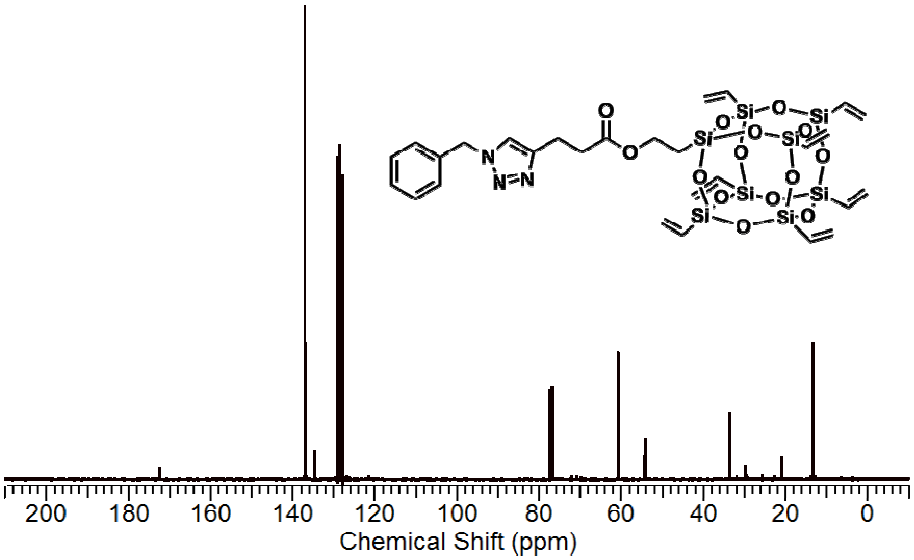


Figure S7. ^{13}C NMR spectrum of Benzyl-VPOSS.

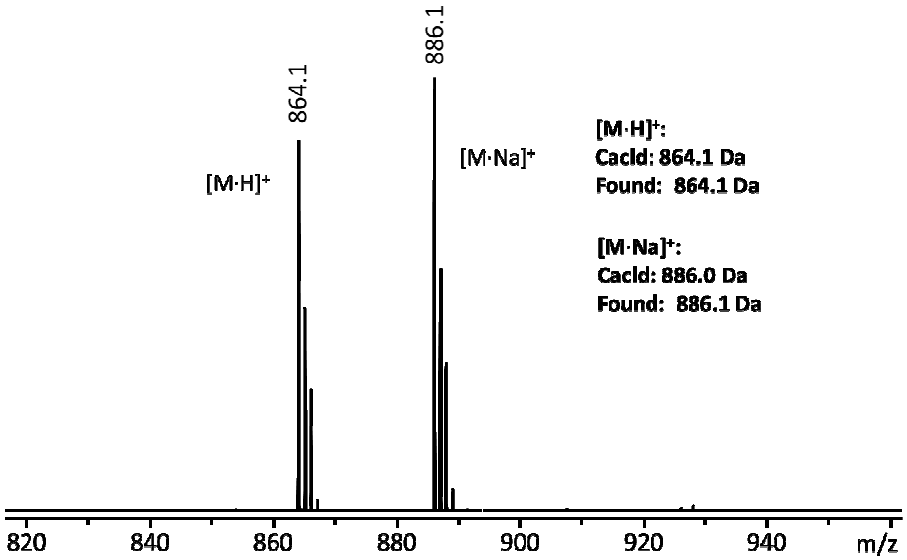


Figure S8. MALDI-TOF MS spectrum of Benzyl-VPOSS.

Reference

(S1). Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413-414.