POSS Dendrimers Constructed from a 1→7 Branching Monomer

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1. Materials

Octavinyl POSS (98%, Hybrid Plastics), 3-mercaptopropionic acid (99%, J&K), trifluoromethanesulfonic acid (99%, Aldrich), 2-mercaptoethylamine hydrochloride (99%, Energy Chemical), 4-(dimethyl-amino)-pyridine (DMAP, 99%, Aldrich), 1-(3-dimethylaminopropyl) -3-ethylcarbodiimide hydrochloride (99%, Energy Chemical), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, J&K), succinic anhydride (99%, J&K), triethylamine (TEA, 99%, Beijing Chemical Works), methanol, hydrochloric acid, hexane and ether (reagent grade, Beijing Chemical Works), tetrahydrofuran (THF), N,N-dimethyl formamide (DMF), chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) were purified by stirring over calcium hydride for 24 h followed by distillation.

2. Characterizations

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by drop-casting sample films on a KBr plate from a polymer solution in chloroform with subsequent drying by infrared lamp. All NMR spectra were obtained on a Bruker DRX-400 spectrometer. Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments, Inc., MDSC-2910. The temperature program was from 60 to 700 ℃ with an increasing rate of 10 ℃ min^{-1} in a flow of air. Transmission electron microscopy (TEM) images were obtained on a JEM-2200FS microscope (JEOL, Japan). Atomic force microscopy (AFM) images were obtained on a Nanoscope Multimode III AFM instrument (Vecco, America) in tapping mode. Dynamic light scattering (DLS) spectra were obtained in THF on a commercial laser light scattering spectrometer (ALV/DLS/ SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser (λ_0=632.8 nm), and the angle of 155^0 was used. The laser light scattering cell is held in a thermostat index matching vat filled with purified and dust-free toluene, with the temperature controlled to within 0.1 ℃. MALDI-TOF-MS measurement was carried out using a Bruker BIFLEX III equipped with a 337 nm nitrogen laser. Gel permeation chromatography (GPC) measurements were carried out on GPCmax VE-2001 (Viscotek) equipped with a Viscotek TriSEC Model 302 triple detector array (refractive index detector, viscometer detector, and laser light scattering detector (7^0 and 90^0)) using two I-3078 Polar Organic Columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. Absolute molecular weights (M_n and M_w) and polydispersity indexes (PDIs) were obtained using the workstation software equipped with the system by the processing method for dendritic polymers based on a working curve of polystyrene standards.

3. Syntheses of the POSS core, monomer and dendrimers

Synthesis of the septvinyl monohydroxyl POSS, (Vinyl)$_7$-POSS-OH: To a solution of octavinyl POSS (2 g, 3.159 mmol) in 300 mL of fresh distilled CH_2Cl_2, trifluoromethanesulfonic acid (0.280 mL, 3.159 mmol) was slowly added dropwise via syringe at room temperature. After 4 hours, the solution was diluted with CH_2Cl_2 and then washed with saturated aqueous Na_2CO_3 three times. The organic layer was then concentrated by evaporating the excess solvent. Then wet acetone was added into the

concentrated solution and the hydrolysis process was performed for 4 h. The crude product was yielded after removing the solvent. The final product was separated chromatographically on silica gel with CH_2Cl_2/hexane (v/v = 2/1) to afford a white solid, (Vinyl)$_7$-POSS-OH, (604 mg, 29.2 %) after obtained in vacuo.

Synthesis of the octaamine POSS, POSS-(NH$_3$Cl)$_8$. A 250 ml round-bottom flask was charged with a mixture solution of octavinyl POSS (3.18 g, 5 mmol), cysteamine hydrochloride (11.3 g, 0.1 mol) and DMPA (0.42 g, 1.64 mmol) in 150 mL of THF/MeOH (v/v = 3/1). The mixture was purged with argon for 15 min and then irradiated under a 365 nm UV lamp at room temperature for 3 h. A mount of white precipitate was collected by filtration and washed with a mixture of THF/MeOH (v/v = 5/1) five times to afford a white powder, POSS-(NH$_3$Cl)$_8$, (6.5 g, 84.4%) after obtained in vacuo.

Synthesis of the octa-(carboxylic acid) POSS, POSS-(COOH)$_8$. To a solution of POSS-(NH$_3$Cl)$_8$ (1.31 g, 0.85 mmol) and triethylamine (1 mL, 7.2 mmol) in MeOH (15 mL), succinic anhydride (1.5 g, 15.0 mmol) was added, and the mixture was stirred at room temperature. After 2 h, chloroform was poured into the solution, and the white precipitate was collected via filtration and washed with chloroform as a white powder, POSS-(COOH)$_8$, (1.37 g, 79%) after obtained in vacuo.

Synthesis of the G1 POSS dendrimer, POSS$_9$-(Vinyl)$_{56}$. (Vinyl)$_7$-POSS-OH (975 mg, 1.5 mmol), POSS-(COOH)$_8$ (307.2 mg, 0.15 mmol), EDCI (345.6 mg, 1.8 mmol) and DMAP (33.6 mg, 0.3 mmol) were added to a 100 mL round-bottomed flask equipped with a magnetic stirring bar, followed by the addition of 30 mL of freshly dried DMF to fully dissolve all the solids. The solution was cooled to 0 ℃ for 15 min and allowed to the room temperature, and then further stirred for another 24 h to complete the reaction. After removing DMF, ethyl acetate was added to dissolve the white solids, and then washed with 2M HCl aqueous solution, saturated NaCl aqueous solution and DI water for three times and dried over anhydrous Na$_2$SO$_4$. Then the final product was precipitated into hexane several times to remove the excess (Vinyl)$_7$-POSS-OH to afford the white powder, POSS$_9$-(Vinyl)$_{56}$, (0.64 g, 60%) after obtained in vacuo.

Synthesis of the G1.5 POSS dendrimer, POSS$_9$-(COOH)$_{56}$. POSS$_9$-(Vinyl)$_{56}$ (0.32 g, 0.04 mmol), 3-mercaptopropionic acid (0.51 g, 4.8 mmol), and DMPA (42 mg, 0.16 mmol) were dissolved in 10 mL of THF. After irradiation under a 365 nm UV lamp at room temperature for 4 h to make sure no vinyl groups existed. The product was precipitated into ether several times to remove the excess 3-mercaptopropionic acid to afford the yellowish powder, POSS$_9$-(COOH)$_{56}$, (0.3 g, 57.6%) after obtained in vacuo.

Synthesis of the G2 POSS dendrimer, POSS$_{65}$-(Vinyl)$_{392}$. (Vinyl)$_7$-POSS-OH (1.5 g, 2.3 mmol), POSS$_9$-(COOH)$_{56}$ (0.3 g, 0.023 mmol), EDCI (0.53 g, 2.76mmol) and DMAP (51 mg, 0.46 mmol) were added to a 100 mL round-bottomed flask equipped with a magnetic stirring bar, followed by the addition of 30 mL of freshly dried DMF to fully dissolve all the solids. The solution was cooled to 0 ℃ for 15 min and allowed to the room temperature, and then further stirred for another 24 h to

complete the reaction. After removing DMF, ethyl acetate was added to dissolve the white solids, and then washed with 2M HCl aqueous solution, saturated NaCl aqueous solution and DI water for three times and dried over anhydrous Na_2SO_4. Then the final product was precipitated into hexane several times to remove the excess $(Vinyl)_7$-POSS-OH to afford the white powder, $POSS_{65}$-$(Vinyl)_{392}$, (0.23 g, 20.7%) after obtained in vacuo.

4. Calculation methods

The geometries of the G0-G2 POSS dendrimers were optimized in the gas phase by Semi-empirical quantum chemical method using the PM6,[1] which consists of an optimization of a large set of parameters that included 70 elements and obtained an improvement in accuracy. The PM6 can yield reliable results for large molecular structures at lower computational costs than those related to more sophisticated ab initio approaches. All the calculations were carried out using the Gaussian 09 program package.[2] To further understand the structures and dimensions of the G0-G2 POSS molecules, a molecular mechanic simulation was also employed in this work. The condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field was adopted to perform energy minimization.[3] The radius of the molecule is defined as the distance between the center of the central POSS and the farthest carbon atom in the simulation.

The branches of the POSS molecule should be extended because of the steric hindrance in equilibrium state. In this simulation, the conformation of the POSS molecule is obtained by molecular mechanics (MM) method. It should be noted that the conformation energy may not be minimum globally but locally due to the limit of exploring phase space. In other words, the branches of POSS molecule in our simulation may not all extended. However, we know that the extended branch represents the real state for the POSS molecule in equilibrium state. So we calculate the radial distribution function (RDF) of the center in the POSS molecule and the outside carbon atoms after the MM process. And the longest distance in the RDF plot, or the farthest distance for the two sorts of atoms, would be the maximum radius of the POSS molecule. RDF was calculated based on the below equation:

$$g_{ab}(r) = \frac{1}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \left\langle \delta \left| r_{ij} \right| - r \right\rangle$$

Where a, b represent two sorts of atoms, and they also could be same. δ is delta function.

1. J. J. P. *J.* Stewart, *Mol. Model.*, 2007, **13**, 1173.
2. G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, M. Caricato and X. Li, Gaussian 09, revision B. 01; Gaussian. *Inc., Wallingford, CT*, 2009.
3. H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338.
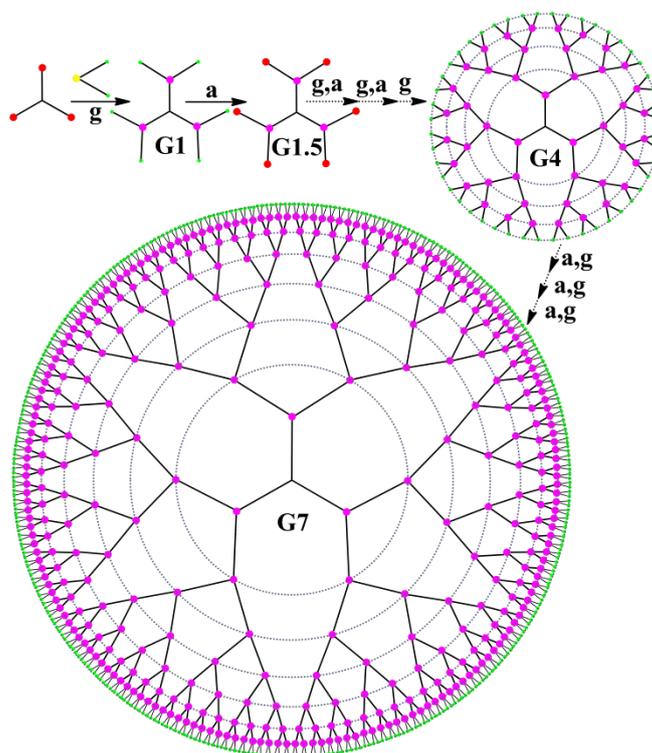
Fig. S1 Schematic illustration of a traditional divergent approach to the dendrimers starting from a tri-functional core and an AB_2 monomer.

$POSS_9\text{-}(Vinyl)_{56}$
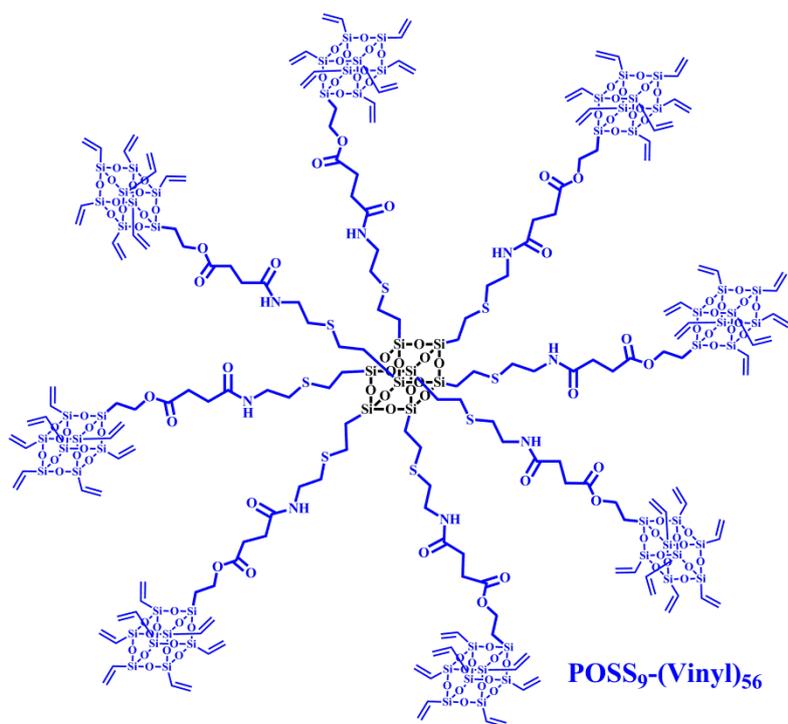
Fig. S2 Chemical structure of the G1 POSS dendrimer.
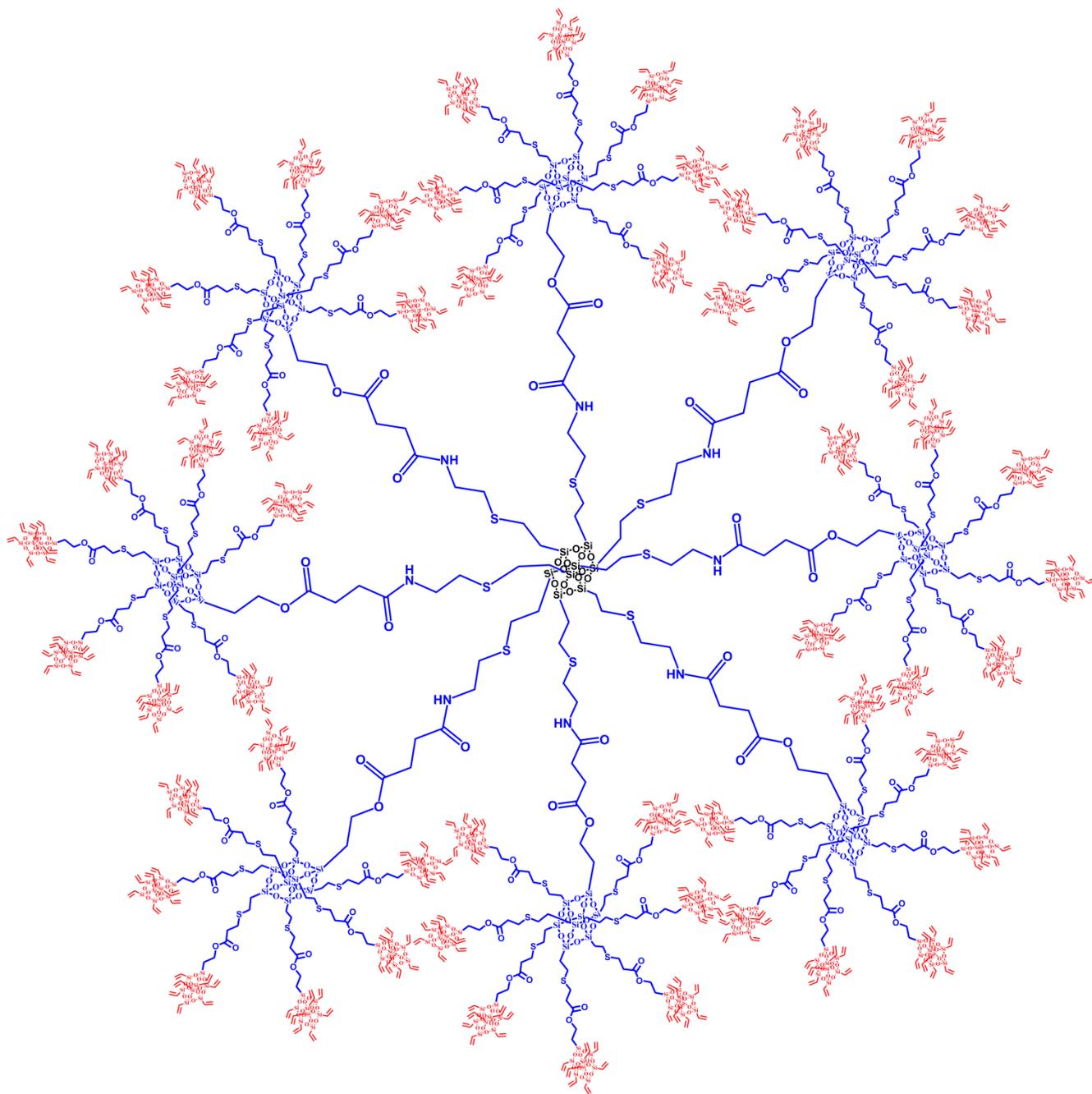
Fig. S3 Chemical structure of the G2 POSS dendrimer.
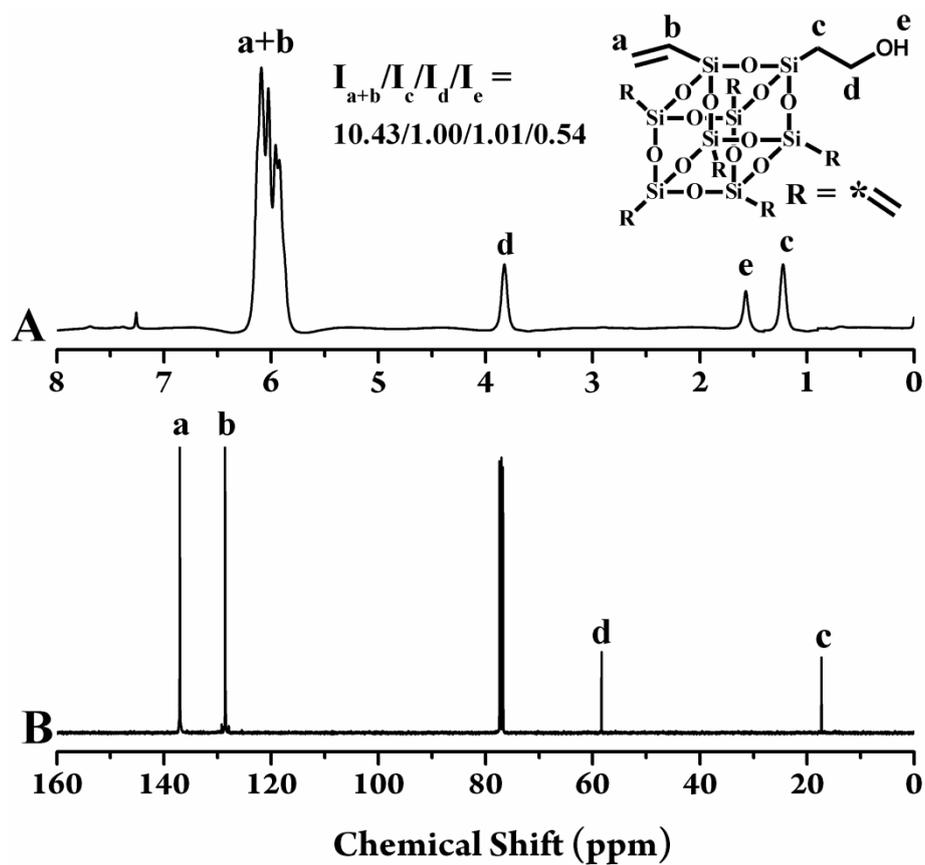
Fig. S4 (A) ^{1}H and (B) ^{13}C NMR spectra of the AB$_7$ monomer, (Vinyl)$_7$-POSS-OH, at CDCl$_3$.
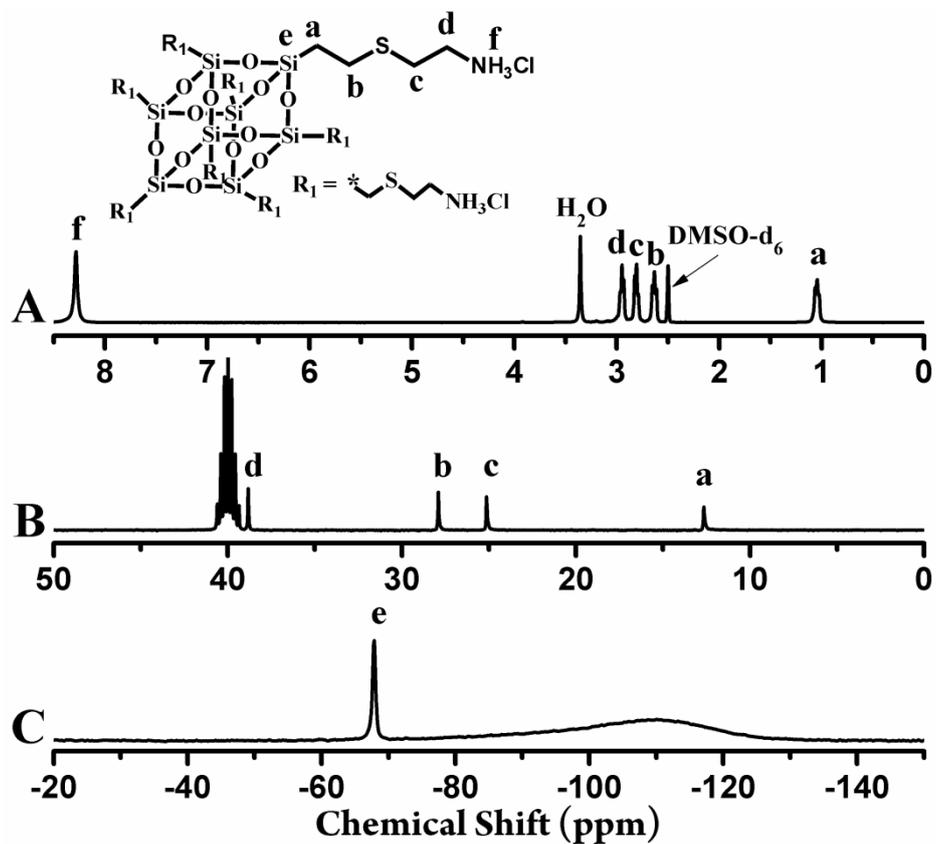
Fig. S5 (A) ^{1}H, (B) ^{13}C and ^{29}Si NMR spectra of the octaammonium POSS, POSS-(NH$_3$Cl)$_8$, at DMSO-d$_6$.
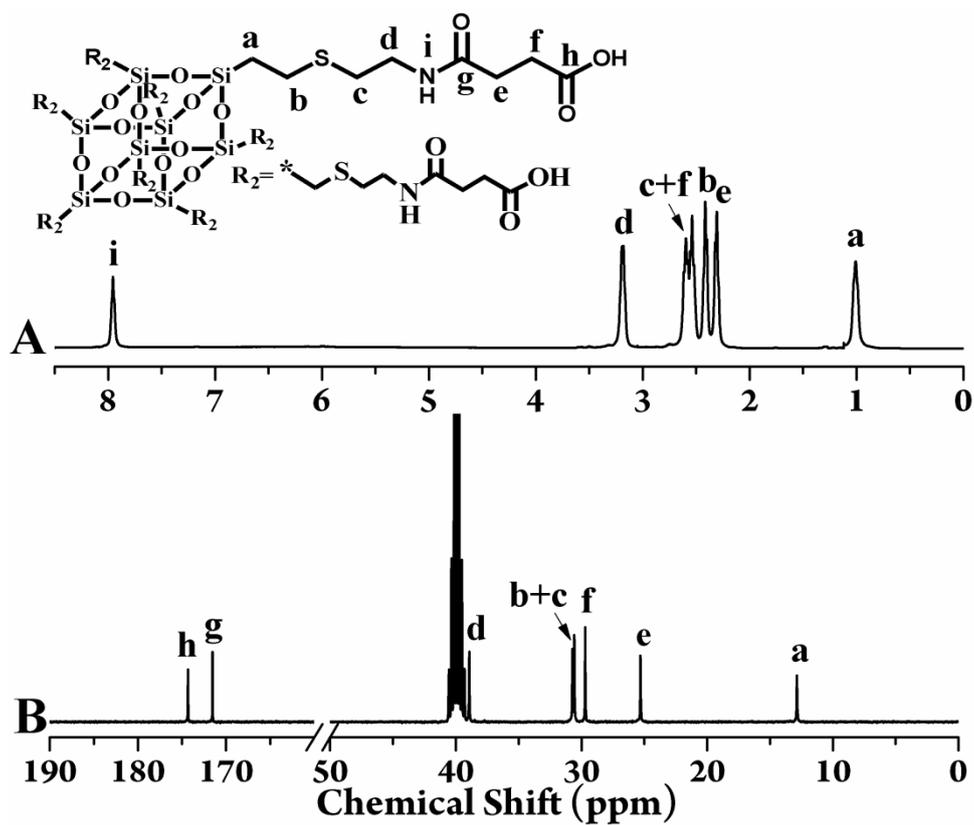
Fig. S6 (A) ^{1}H and (B) ^{13}C NMR spectra of the octa(carboxylic acid) POSS, POSS-(COOH)$_8$, at DMSO-d$_6$.
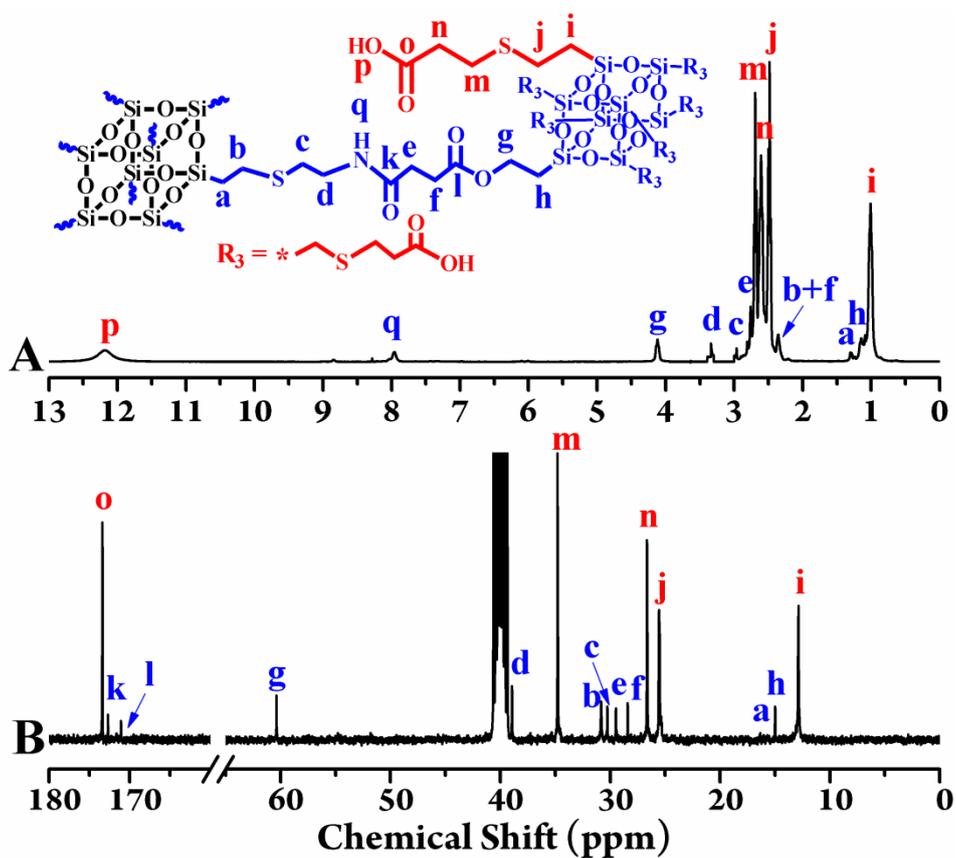
Fig. S7 (A) ^{1}H and (B) ^{13}C NMR spectra of the G1.5 POSS dendrimer, POSS$_9$-(COOH)$_{56}$, at DMSO-d$_6$.
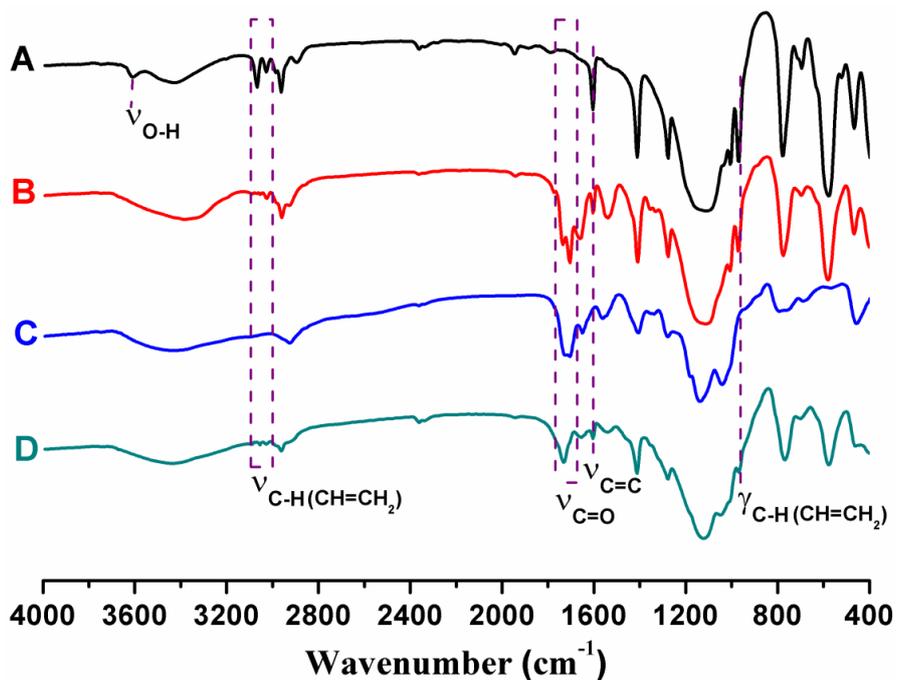
Fig. S8 IR spectra of the (A) AB$_7$ monomer, (B) G1, (C) G1.5 and (D) G2 POSS dendrimers.
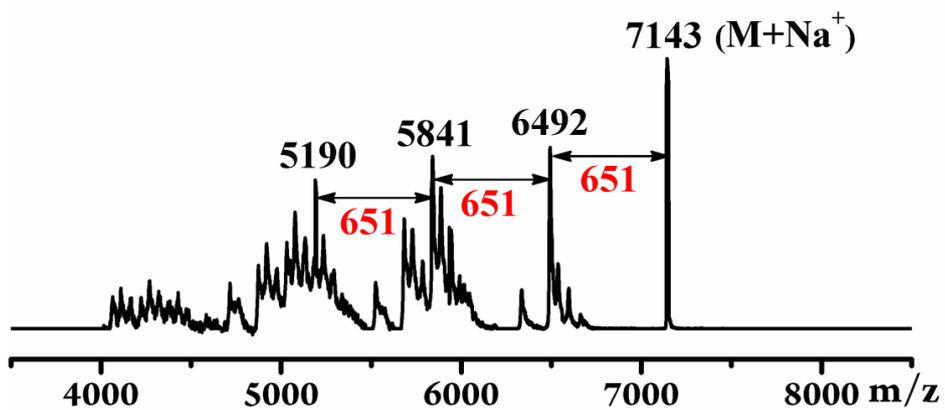
Fig. S9 MALDI-TOF spectrum of the G1 POSS dendrimer (M+Na$^+$).
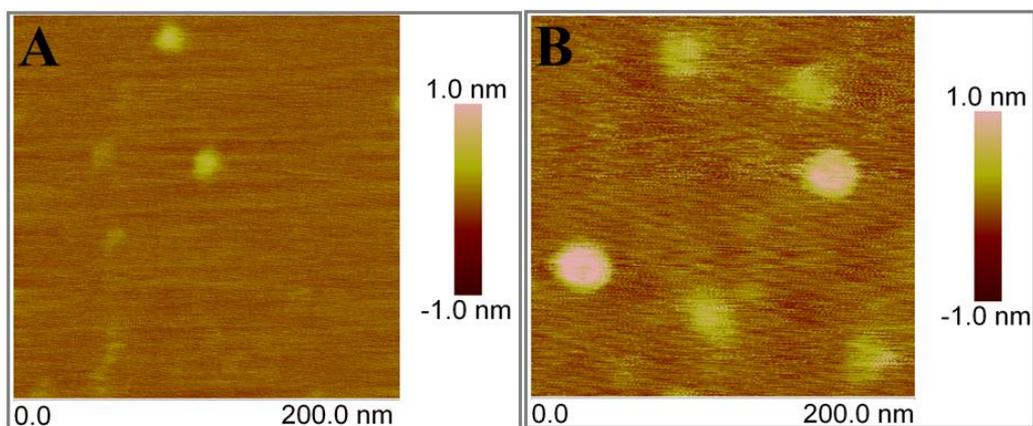
Fig. S10 AFM images of the (A) G1 and (B) G2 POSS dendrimers.
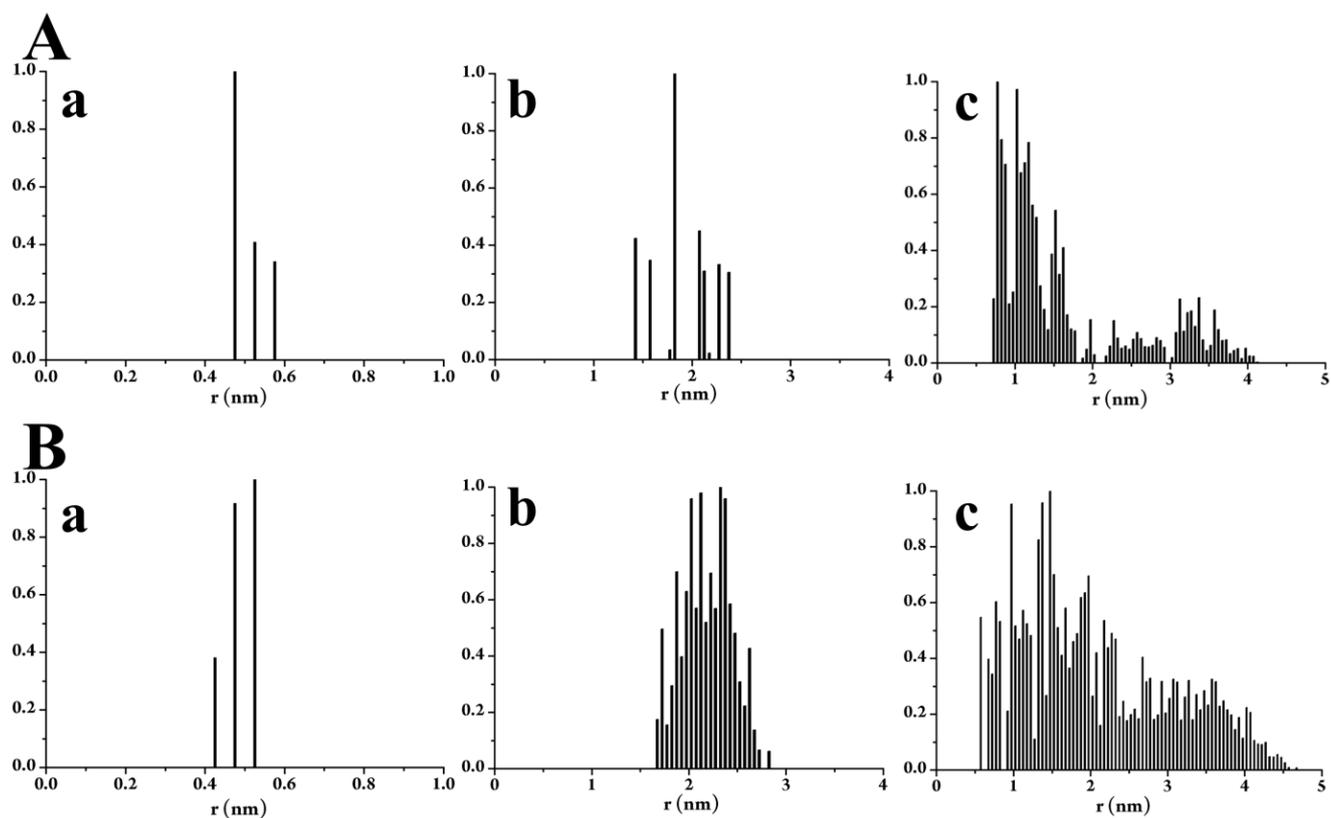
Fig. S11 Radial distribution functions of the center of the dendrimers and the outer layer of carbon atoms of the (a) G0, (b) G1 and (c) G2 POSS dendrimers derived from (A) quantum chemical method and (B) molecular mechanic calculation.

Table S1. Theoretic molecular sizes of the G0, G1 and G2 POSS dendrimers

Methods	R_g (radius of gyration) (nm)			r (radius) (nm)		
	G0 POSS	G1 POSS	G2 POSS	G0 POSS	G1 POSS	G2 POSS
Quantum Chemical Method (QCM)	0.47	1.71	2.54	0.57	2.37	4.14
Molecular Mechanic Calculation (MMC)	0.47	2.24	2.81	0.53	2.81	4.77