Tuning "Thiol-Ene" Reactions toward Controlled Symmetry Breaking in Polyhedral Oligomeric Silsesquioxanes

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Experimental Section

Materials and Instrumentation. Tetrahydrofuran (THF, EM Science, Certified ACS), methanol (Fisher Scientific, reagent grade), ethyl acetate (EtOAc, Fisher Scientific, ACS grade), acetone (Fisher Scientific, Certified ACS), dichloromethane (Fisher Scientific, Certified ACS), chloroform (Fisher Scientific, Certified ACS), *N*, *N*-dimethylformamide (DMF, Sigma-Aldrich, anhydrous 99.8 %), and hexanes (Fisher Scientific, Certified ACS) were used after distillation. Octavinyl POSS (Hybrid Plastics, > 97 %), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99 %), 2-mercaptoethanol (Aldrich, > 99 %), 6-mercapto-1-hexanol (Sigma, 97 %), 1-thioglycerol (Sigma, > 99 %), 2-(Boc-amino)ethanethiol (Sigma, 97 %), 1-thio-β-d-glucose tetraacetate (Sugar-SH, Alfa Aesar, 99%), 2-hydroxyethyl disulfide (Sigma, technical grade), DL-dithiothreitol (DTT, Sigma, > 99 %), 2-bromoisobutyryl bromide (Aldrich, 98 %), triethylamine (TEA, Sigma, > 99 %), *N*, *N*′-diisopropylcarbodiimide (DIPC, Acros Organics, 99 %), 4-(dimethylamino) pyridine (DMAP, Aldrich, 99 %), sodium azide (Aldrich, > 99 %), 4-(bromomethyl)benzoic acid (Sigma, 97 %), succinic anhydride (Sigma, > 99 %), 1-adamantanemethanol (Sigma, 99 %), ferrocenecarboxylic acid (Aldrich, 97 %), aminopropylIsobutyl POSS (Hybrid Plastics, 99 %), 4′-hydroxy-4-biphenylcarbonitrile (Aldrich, 97 %), 1,6-dibromohexane (Aldrich, 96 %), potassium carbonate (Sigma, > 99 %), potassium thioacetate (Aldrich, 98 %), sodium methoxide solution (25 wt. % in methanol, Aldrich), ammonium chloride (Aldrich, 99 %), 1-bromopentane (Aldrich, 98 %), methyl 3,4,5-trihydroxybenzoate (Aldrich, 98 %), PSS-(3-mercapto)propyl-heptaisobutyl substituted (BPOSS-SH, Sigma, 98 %), and potassium hydroxide (Aldrich, 90 %) were used as received. 2-Mercaptoacetic acid (Aldrich, > 98 %) was distilled under reduced pressure before use. Silica gel (VWR, 230-400 mesh) was activated by

heating to 140 °C for 12 hrs. Ultraviolet (UV) light irradiation of the samples was carried out with a 15 W UVP Black Ray UV bench lamp XX-15 L, emitting around 365 nm wavelength (intensity ca. 4.6 mW cm^{-2}).

Characterization. All ^{1}H, ^{13}C and ^{29}Si NMR spectra were acquired in $CDCl_3$ (Aldrich, 99.8 % D) utilizing a Varian Mercury 300 NMR and 500 NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton signals in $CDCl_3$ at δ 7.27 ppm; while the ^{13}C NMR spectra were referenced to $^{13}CDCl_3$ at δ 77.00 ppm. And the ^{29}Si NMR spectra were referenced to tetramethylsilane in $CDCl_3$ at δ 0 ppm.

Infrared spectra were obtained on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting films on KBr plates from solutions with subsequent drying at 40 - 50 °C. The spectroscopic data were processed using Win-IR software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All spectra were measured in positive reflection or linear mode. The instrument was calibrated prior to each measurement with external poly(methyl methacrylate), PMMA, or polystyrene, PS, standards at the molecular weight under consideration. The compound *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Santa Cruz Biotechnology, Inc., >99 %) served as matrix and was dissolved in $CHCl_3$ at a concentration of 20 mg/mL. The cationizing agent, sodium trifluoroacetate or silver trifluoroacetate, was dissolved in MeOH/$CHCl_3$ (v/v = 1/3) at a concentration of 5 mg/mL or 10 mg/mL. All samples were dissolved in $CHCl_3$. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). The sample preparation followed the procedure of depositing 0.5 μL of matrix and salt mixture

on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix/salt, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample (sandwich method). After solvent evaporation, the plate was inserted into the MALDI mass spectrometer. The attenuation of the Nd:YAG laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity.

Thin-layer chromatographic analyses of the functionalized polymers were carried out by spotting samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator) and developing using toluene or its mixture with other polar solvents.

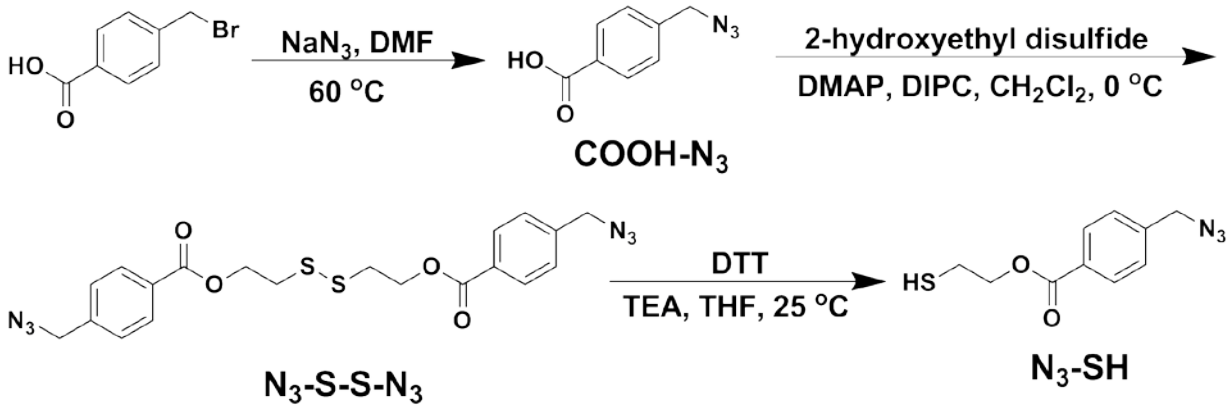
ESI-TWIM MS. Both electrospray ionization mass spectrometry (ESI MS) and ESI-travelling wave ion mobility (TWIM) MS experiments were performed on a Waters Synapt HDMS instrument quadrupole/time-of-flight (Q/ToF) mass spectrometer (Waters, Milford, MA). The tri-wave region of this instrument, located between the Q and ToF mass analyzers, contains three confined regions in the order trap cell (closest to Q), TWIM cell, and transfer cell (closest to ToF). The following ESI and TWIM parameters were selected: ESI capillary voltage, 3.5 kV; sample cone voltage, 35 V; extraction cone voltage, 3.2 V; desolvation gas flow, 500 L/h (N_2); trap collision energy (CE), 6 eV; transfer CE, 4 eV; trap gas flow, 1.5 mL/min (Ar); TWIM gas flow, 22.7 mL/min (N_2); sample flow rate, 5 μL/min; source temperature, 100 °C; desolvation temperature, 150 °C; traveling wave velocity, 350 m/s; traveling wave height, 10 V. The sprayed solutions were prepared by dissolving 0.3 mg of sample in 1 mL of $CHCl_3$/MeOH (v/v, 50/50) containing 1% (v/v) NaTFA solution (1 mg/mL in methanol). Data analysis was conducted with the MassLynx 4.1 and DriftScope 2.1 programs of Waters.

Collision Cross-Sections. The drift time of a specific ion through the TWIM cell can be converted to a collision cross-section, which represents a measure of the ion's size and architecture. With TWIM, collision cross-sections must be deduced by calibrating the drift time scale with ions of known cross-section. Polyalanine ions and a peptide (*viz.* TRQARRNAAAAWRERQR) with established collision cross-sections[1-3] served as standards,[4-6] which were analyzed with the traveling wave velocity, traveling wave height, and TWIM gas flow set at 350 m/s, 10 V, and 22.7 mL/min, respectively. Our calibration curve was constructed by plotting the corrected collision cross-sections of polyalanine and the synthesized peptide ions against the corresponding corrected drift times (arrival times) measured in our experiments.

Molecular Modeling. Molecular modeling of VPOSS-(S-BPOSS)$_2$ was performed by the Materials Studio program (version 4.2), using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). Energy-minimized structures of oxidized tri-POSS were built using 400 anneal cycles with initial and mid-cycle temperatures of 50 and 1400 K, twenty heating ramps per cycle, one thousand dynamics steps per ramp, and one dynamics step per femtosecond. A constant volume/constant energy (NVE) ensemble was used and the geometry was optimized after each cycle. Geometry optimization utilized a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters. 300 energy-minimized structures were selected for the calculation of theoretical collision cross-sections (CCSs) with the MOBCAL program. MOBCAL permits CCS calculations by the projection approximation (PA), trajectory (TJ), and exact hard sphere scattering (EHSS) methods.

Synthetic Procedures

Br-SH (6). Br-SH was synthesized as reported.[7] ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 4.45 (t, 2H, -C$\underline{H}_2$COO-), 2.99 (t, 2H, HSC$\underline{H}_2$-), 1.95 (s, 6H, -CC$_2\underline{H}_6$Br).



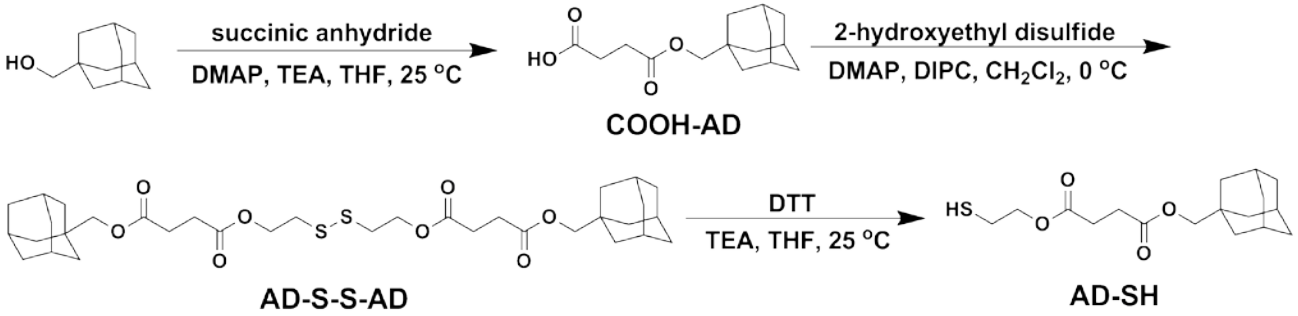
Scheme S1. Synthetic route for N_3-SH **7**. (DMAP: 4-(dimethylamino) pyridine; DIPC: *N*, *N'*-diisopropylcarbodiimide; DTT: DL-dithiothreitol; TEA: triethylamine.)

N_3-COOH. N_3-COOH was synthesized as reported.[8] ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.15 (d, 2H, -OCCC$_2\underline{H}_2$-), 7.45 (d, 2H, -CH$_2$C$_2\underline{H}_2$-), 4.46 (s, 2H, -C$\underline{H}_2$N$_3$).

N_3-S-S-N_3. COOH-N_3 (372 mg, 2.1 mmol), 2-hydroxyethyl disulfide (154 mg, 1.0 mmol), and DMAP (590 mg, 2.0 mol) were added to a 100 mL round-bottom flask equipped with a magnetic stirring bar, followed by the addition of 20 of mL freshly dried CH_2Cl_2 to fully dissolve the samples. The mixture was capped by a rubber septum, cooled to 0 ^{o}C, and stirred at that temperature for 10 min, and then DIPC (278 mg, 3.0 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hours. The white precipitate was then filtered off and the filtrate was washed with water and brine and dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using CH_2Cl_2 as the eluent to afford the product (369 mg, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.07 (d, 4H, -OCCC$_2\underline{H}_2$-), 7.39 (d, 4H, -CH$_2$C$_2\underline{H}_2$-), 4.61 (t, 4H, -C$\underline{H}_2$COO-), 4.42 (s, 4H, -C$\underline{H}_2$N$_3$), 3.10 (t, 4H,

-SC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 165.81, 140.67, 130.22, 129.98, 127.94, 62.81, 54.27, 37.39.

N_3-SH (7). N_3-S-S-N_3 (200 mg, 0.423 mmol), DTT (78 mg, 0.508 mmol), and TEA (214 mg, 2.12 mmol) were completely dissolved in 20 mL of THF. The solution was stirred at room temperature for 4 h. THF was evaporated under vacuum and 50 mL CH_2Cl_2 were used to dissolve the crude sample. The solution was then washed three times with water. The organic layer was dried over anhydrous Na_2SO_4 overnight and evaporated under vacuum after filtration. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/1) as eluent to afford the targeted product (160 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.07 (d, 2H, -OCCC$_2$<u>H</u>$_2$-), 7.40 (d, 2H, -CH$_2$C$_2$<u>H</u>$_2$-), 4.45 (t, 2H, -C<u>H</u>$_2$COO-), 4.42 (s, 2H, -C<u>H</u>$_2$N$_3$), 2.90 (t, 2H, HSC<u>H</u>$_2$-), 1.56 (t, 1H, -S<u>H</u>). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 165.41, 140.67, 130.16, 129.95, 127.96, 66.24, 54.24, 23.38.



Scheme S2. Synthetic route for AD-SH **8**. (DMAP: 4-(dimethylamino) pyridine; TEA: triethylamine; DIPC: *N, N'*-diisopropylcarbodiimide; DTT: DL-dithiothreitol.)

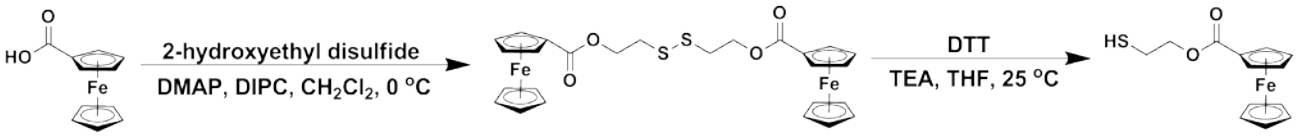
COOH-AD. A 100 mL, round-bottom flask was charged with a solution of 1-adamantanemethanol (300 mg, 1.80 mmol) in 20 mL fresh distilled THF. To this stirred solution, succinic anhydride (894 mg, 9.00 mmol), DMAP (1088 mg, 9.00 mmol), and TEA (1821 mg, 18.00 mmol) were added at room temperature. After stirring overnight, the mixture was quenched by 2 M

aqueous HCl solution. The solution was then washed with water three times and dried over anhydrous Na_2SO_4. After removal of the solvent, the product was purified chromatographically on silica gel with CH_2Cl_2/EtOAc (v/v = 20/1) to give COOH-AD (427 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 3.71 (s, 2H, -COOC$\underline{H}_2$-), 2.71-2.61 (m, 4H, HOOCC$_2\underline{H}_4$-), 1.98 [m, 3H, -C(CH$_2$C$\underline{H}$)$_3$-], 1.75-1.53 [m, 12H, -C(C$\underline{H}_2$CHC$\underline{H}_2$-)$_3$]. ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 177.70, 172.14, 74.42, 39.19, 36.92, 33.19, 28.96, 28.02, 24.61.

AD-S-S-AD. COOH-AD (559 mg, 2.1 mmol), 2-hydroxyethyl disulfide (154 mg, 1.0 mmol), and DMAP (590 mg, 2.0 mol) were added to a 100 mL round-bottom flask equipped with a magnetic stirring bar, followed by the addition of 20 mL freshly dried CH_2Cl_2 to fully dissolve the samples. The mixture was capped by a rubber septum, cooled to 0 ^{o}C, and stirred at that temperature for 10 min, and then DIPC (278 mg, 3.0 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hours. The white precipitate was then filtered off and the filtrate was washed with water and brine and dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using CH_2Cl_2 as the eluent to afford the product (488 mg, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 4.31 (t, 4H, -SCH$_2$C$\underline{H}_2$-), 3.64 (s, 4H, -COOC$\underline{H}_2$C-), 2.88 (t, 4H, -SC$\underline{H}_2$CH$_2$-), 2.63-2.53 (m, 8H, -OOCC$_2\underline{H}_4$-), 1.94 [m, 6H, -C(CH$_2$C$\underline{H}$)$_3$-], 1.71-1.48 [m, 24H, -C(C$\underline{H}_2$CHC$\underline{H}_2$-)$_3$]. ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 172.11, 74.23, 62.45, 39.17, 36.90, 33.13, 29.06, 27.98, 14.15.

AD-SH (8). AD-S-S-AD (300 mg, 0.461 mmol), DTT (85 mg, 0.553 mmol), and TEA (233 mg, 2.31 mmol) were completely dissolved in 20 mL of THF. The solution was stirred at room temperature for 4h. THF was evaporated under vacuum and 50 mL CH_2Cl_2 were used to dissolve the crude sample. The solution was then washed three times with water. The organic layer was

dried over anhydrous Na_2SO_4 overnight and evaporated under vacuum after filtration. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/4) as eluent to afford the targeted product (252 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 4.21 (t, 2H, $HSCH_2C\underline{H}_2$-), 3.69 (s, 2H, -$COOC\underline{H}_2C$-), 2.74 (m, 2H, $HSC\underline{H}_2CH_2$-), 2.68-2.59 (m, 4H, -$OOCC_2\underline{H}_4$-), 1.96 [m, 3H, -$C(CH_2C\underline{H})_3$-], 1.74-1.47 [m, 12H, -$C(C\underline{H}_2CHC\underline{H}_2$-$)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 172.21,171.93, 74.32, 65.92, 39.21, 36.93, 33.16, 29.10, 28.01, 23.20.

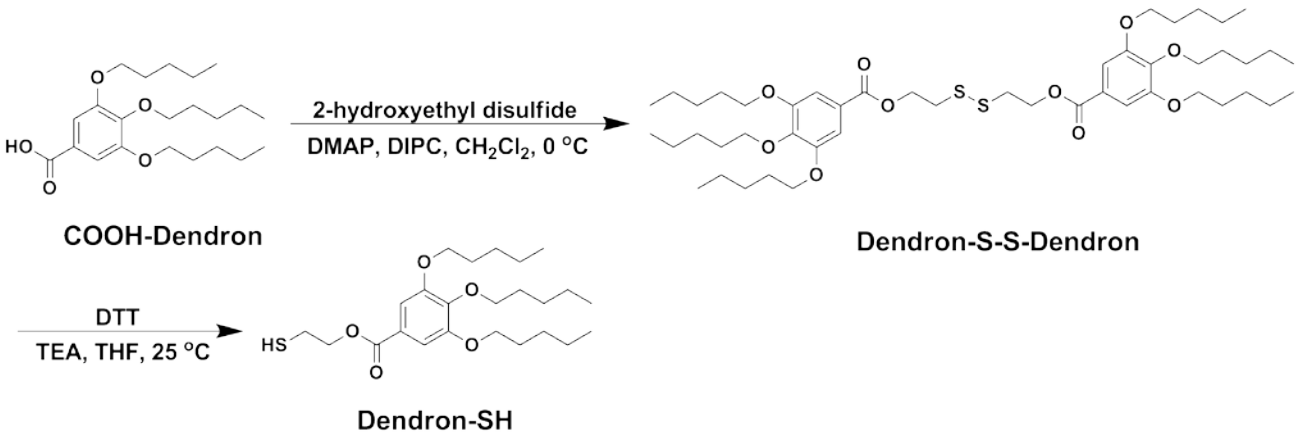


Fe-S-S-Fe Fe-SH

Scheme S3. Synthetic route for Fe-SH **9**. (DMAP: 4-(dimethylamino) pyridine; DIPC: *N*, *N'*-diisopropylcarbodiimide; DTT: DL-dithiothreitol; TEA: triethylamine.)

Fe-S-S-Fe. Ferrocenecarboxylic acid (483 mg, 2.1 mmol), 2-hydroxyethyl disulfide (154 mg, 1.0 mmol), and DMAP (590 mg, 2.0 mol) were added to a 100 mL round-bottom flask equipped with a magnetic stirring bar, followed by the addition of 20 mL freshly dried CH_2Cl_2 to fully dissolve the samples. The mixture was capped by a rubber septum, cooled to 0 ^{o}C and stirred at that temperature for 10 min, and then DIPC (278 mg, 3.0 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hours. The white precipitate was then filtered off and the filtrate was washed with water and brine and dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using CH_2Cl_2 as the eluent to afford the product (445 mg, 77 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 4.83 (m, 4H, C_5H_2), 4.52 (t, 4H, -$SCH_2C\underline{H}_2$-), 4.41 (m, 4H, C_5H_4), 4.23 (s, 10H, C_5H_5), 3.09 (t, 4H, -$SC\underline{H}_2CH_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 171.55, 71.42, 70.89, 70.20, 69.84, 61.98, 37.71, 23.49.

Fe-SH (9). Fe-S-S-Fe (250 mg, 0.432 mmol), DTT (80 mg, 0.519 mmol), and TEA (218 mg, 2.16 mmol) were completely dissolved in 20 mL of THF solution. The solution was stirred at room temperature for 4 h. THF was evaporated under vacuum and 50 mL CH_2Cl_2 were used to dissolve the crude sample. The solution was then washed three times with water. The organic layer was dried over anhydrous Na_2SO_4 overnight and evaporated under vacuum after filtration. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/10) as eluent to afford the targeted product (220 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 4.81 (m, 2H, C_5H_2), 4.39 (m, 2H, C_5H_2), 4.32 (t, 2H, $HSCH_2C\underline{H}_2$-), 4.20 (s, 5H, C_5H_5), 2.83 (m, 2H, $HSC\underline{H}_2$-), 1.56 (t, 1H, $\underline{H}SCH_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 171.37, 71.43, 70.72, 70.15, 69.83, 65.41, 23.58.



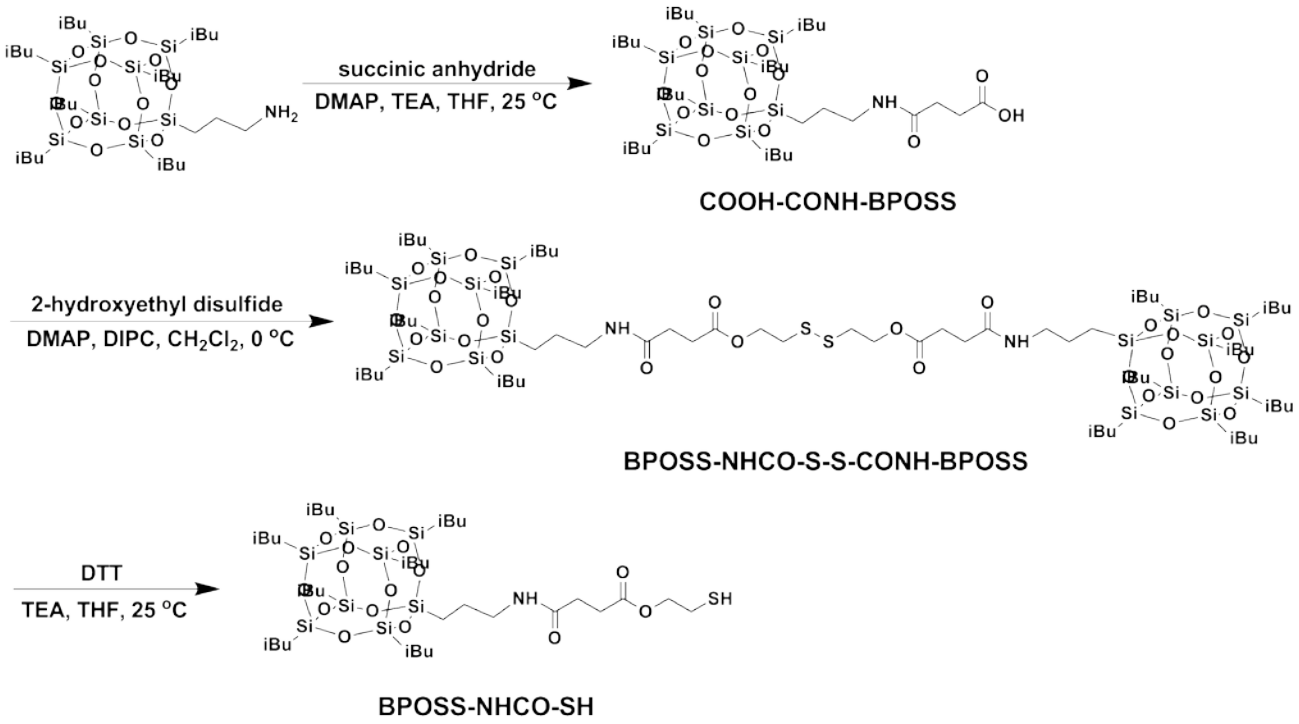
Scheme S4. Synthetic route for Dendron-SH **11**. (DMAP: 4-(dimethylamino) pyridine; DIPC: *N*, *N'*-diisopropylcarbodiimide; DTT: DL-dithiothreitol; TEA: triethylamine.)

COOH-Dendron. The synthesis of COOH-Dendron [3,4,5-Tris(n-pentan-1-yloxy)benzoic acid] was reported in an earlier publication.[9]

Dendron-S-S-Dendron. COOH-Dendron (799 mg, 2.1 mmol), 2-hydroxyethyl disulfide (154 mg, 1.0 mmol), and DMAP (590 mg, 2.0 mol) were added to a 100 mL round-bottom flask equipped

with a magnetic stirring bar, followed by the addition of 20 mL freshly dried CH_2Cl_2 to fully dissolve the samples. The mixture was capped by a rubber septum, cooled to 0 ^oC, and stirred at that temperature for 10 min, and then DIPC (278 mg, 3.0 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hours. The white precipitate was then filtered off and the filtrate was washed with water and brine and dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using EtOAc/CH_2Cl_2 (v/v = 1/2) as the eluent to afford the product (712 mg, 81 %). ^1H NMR (300 MHz, $CDCl_3$, ppm, δ): 7.25 (s, 4H, Ar-H), 4.59 (t, 4H, -$SCH_2C\underline{H}_2$-), 4.03 (m, 12H,-$C\underline{H}_2OPh$), 3.10 (t, 4H, -$SC\underline{H}_2CH_2$-), 1.81 (m, 12H,-$C\underline{H}_2CH_2OPh$), 1.44 (m, 24H, (-$C_2\underline{H}_4C_2H_4O$-), 0.95 (t, 18H, -$CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 166.16, 152.87, 142.69, 124.32, 108.19, 73.45, 69.22, 37.43, 29.96, 28.23, 22.41, 13.99.

Dendron-SH (11). Dendron-S-S-Dendron (400 mg, 0.455 mmol), DTT (84 mg, 0.546 mmol), and TEA (230 mg, 2.28 mmol) were completely dissolved in 20 mL of THF. The solution was stirred at room temperature for 4 h. THF was evaporated under vacuum and 50 mL CH_2Cl_2 were used to dissolve the crude sample. The solution was then washed three times with water. The organic layer was dried over anhydrous Na_2SO_4 overnight and evaporated under vacuum after filtration. The residue was purified by flash column chromatography on silica gel with EtOAc /CH_2Cl_2 (v/v = 1/10) as eluent to afford the targeted product (332 mg, 83%). ^1H NMR (300 MHz, $CDCl_3$, ppm, δ): 7.25 (s, 2H, Ar-H), 4.43 (t, 2H, $HSCH_2C\underline{H}_2$-), 4.03 (m, 6H,-$C\underline{H}_2OPh$), 2.91 (m, 2H, $HSC\underline{H}_2CH_2$-), 1.81 (m, 6H,-$C\underline{H}_2CH_2OPh$), 1.46 (m, 12H, (-$C_2\underline{H}_4C_2H_4O$-), 0.95 (t, 9H, -$CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 166.04, 152.86, 142.71, 124.35, 108.18, 73.46, 69.24, 29.97, 28.22, 23.41, 22.41, 13.99.



Scheme S5. Synthetic route for BPOSS-NHCO-SH **13**. (DMAP: 4-(dimethylamino) pyridine; TEA: triethylamine; DIPC: *N*, *N'*-diisopropylcarbodiimide; DTT: DL-dithiothreitol.)

COOH-CONH-BPOSS. COOH-CONH-BPOSS was synthesized as reported.[10] ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 5.93 (s, 1H, -CONH-), 3.26 (m, 2H, -NHCH_2-), 2.69 (t, 2H, HOOCCH_2-), 2.50 (t, 2H, HOOC CH_2CH_2-), 1.86 (m, 7H, -SiCH_2CHC_2H_6), 1.60 (m, 2H, -NHCH_2CH_2-), 0.94 (d, 42H, -SiCH_2CHC_2H_6), 0.60 (q, 16H, -SiCH_2CH-+-SiCH_2CH_2-).

BPOSS-NHCO-S-S-CONH-BPOSS. COOH-CONH-BPOSS (2.05 g, 2.1 mmol), 2-hydroxyethyl disulfide (154 mg, 1.0 mmol), and DMAP (590 mg, 2.0 mol) were added to a 100 mL round-bottom flask equipped with a magnetic stirring bar, followed by the addition of 35 mL freshly dried CH_2Cl_2 to fully dissolve the samples. The mixture was capped by a rubber septum, cooled to 0 ^{o}C, and stirred at that temperature for 10 min, and then DIPC (278 mg, 3.0 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hours. The white precipitate was then filtered off and the filtrate was washed with water and brine and dried

over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using EtOAc/CH_2Cl_2 (v/v = 1/2) as the eluent to afford the product (1. 49 g, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 5.73 (s, 2H, -CONH-), 4.32 (t, 4H, -SCH_2CH_2-), 3.22 (m, 4H, -$NHCH_2$-), 2.90 (t, 4H, -SCH_2CH_2-), 2.66 (t, 4H, -CH_2CH_2COONH-), 2.44 (t, 4H, -CH_2COONH-), 1.84 (m, 14H, -$SiCH_2CHC_2H_6$), 1.57 (m, 4H, -$NHCH_2CH_2$-), 0.94 (d, 84H, -$SiCH_2CHC_2H_6$), 0.60 (q, 32H, -$SiCH_2CH$-+-$SiCH_2CH_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 172.80, 171.05, 62.55, 42.04, 37.31, 29.62, 25.80, 25.78, 23.99, 23.95, 23.11, 22.62, 22.58, 9.57.

BPOSS-NHCO-SH (13). BPOSS-NHCO-S-S-CONH-BPOSS (400 mg, 0.193 mmol), DTT (36 mg, 0.232 mmol), and TEA (97 mg, 0.965 mmol) were completely dissolved in 30 mL of THF. The solution was stirred at room temperature for 4 h. THF was evaporated under vacuum and 50 mL CH_2Cl_2 were used to dissolve the crude sample. The solution was then washed three times with water. The organic layer was dried over anhydrous Na_2SO_4 overnight and evaporated under vacuum after filtration. The residue was purified by flash column chromatography on silica gel with EtOAc /CH_2Cl_2 (v/v = 1/10) as eluent to afford the targeted product (352 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 5.62 (s, 1H, -CONH-), 4.22 (t, 2H, $HSCH_2CH_2$-), 3.23 (m, 2H, -$NHCH_2$-), 2.79-2.67 (m, 4H, $HSCH_2CH_2$-+-CH_2CH_2COONH-), 2.47 (t, 2H, -CH_2COONH-), 1.86 (m, 7H, -$SiCH_2CHC_2H_6$), 1.55 (m, 2H, -$NHCH_2CH_2$-), 0.96 (d, 42H, -$SiCH_2CHC_2H_6$), 0.60 (q, 16H, -$SiCH_2CH$-+-$SiCH_2CH_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 172.85, 171.10, 66.06, 42.06, 31.13, 29.60, 25.84, 24.04, 24.00, 23.40, 23.13, 22.62, 22.59, 9.58.

General Procedure for the Synthesis of VPOSS-S-R 14-26 Using Thiol-Ene Chemistry. OctavinylPOSS (1.0 equiv), functional thiol ligand **1-13** (R-SH, 1.0 equiv), and DMPA (0.02 equiv) were added to a 50 mL beaker equipped with a magnetic stirring bar and dissolved in a defined

volume of THF solvent. The solution was irradiated under a 365 nm UV lamp at room temperature for 0.5-1 hour. After removal of the solvent, the crude sample was purified by flash column chromatography to afford the final product.

VPOSS-S-OH (14.) OctavinylPOSS (500 mg, 0.790 mmol), 2-mercaptoethanol **1** (62 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/2) as the eluent to afford the product as a white powder (144 mg, 26%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.15-5.85 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 3.71 (t, 2H, -C<u>H</u>$_2$OH), 2.79-2.62 (m, 4H, -C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.08 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 137.01, 128.56, 69.04, 60.02, 41.67, 25.55. MS (MALDI-TOF) (Figure S1): Calcd. *m/z* for $C_{18}H_{30}NaO_{13}SSi_8$ 732.95, Found: 733.15 $(M{\cdot}Na)^+$.

VPOSS-S-C$_6$-OH (15). OctavinylPOSS (500 mg, 0.790 mmol), 6-mercapto-1-hexanol **2** (106 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/2) as the eluent to afford the product as a white powder (139 mg, 23%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.16-5.87 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 3.65 (t, 2H, -C<u>H</u>$_2$OH), 2.43-2.68 (m, 4H, -C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.37-1.63 (m, 8H, -SCH$_2$C$_4$<u>H</u>$_8$-), 1.08 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 137.06, 128.59, 62.92, 35.16, 33.72, 32.64, 29.72, 28.68, 25.38, 12.35. MS (MALDI-TOF) (Figure S2): Calcd. *m/z* for $C_{23}H_{39}NNaO_{14}SSi_8$ 789.01, Found: 789.07 $(M{\cdot}Na)^+$.

VPOSS-S-Di-OH (16). The synthesis of VPOSS-S-Di-OH was reported in our previous manuscript.[11]

VPOSS-S-NH-Boc (17). OctavinylPOSS (500 mg, 0.790 mmol), 2-(Boc-amino)ethanethiol **4** (140 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with EtOAc /CH_2Cl_2 (v/v = 1/1) as the eluent to afford the product as a white powder (128 mg, 20%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.15-5.86 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 4.91 (s, 1H, -N<u>H</u>COO-), 3.31 (t, 2H, -C<u>H</u>$_2$NH-), 2.53-2.82 (m, 4H, -C<u>H</u>$_2$SC<u>H</u>$_2$-), 1.45 (s, 9H, -CC$_3$<u>H</u>$_9$), 1.08 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 163.83, 137.01, 128.63, 57.78, 47.81, 30.28, 29.70, 28.40, 11.87. MS (MALDI-TOF) (Figure S3): Calcd. for $C_{23}H_{39}NNaO_{14}SSi_8$ 832.01, Found: 832.11 $(M{\cdot}Na)^+$; Calcd. *m/z* for $C_{23}H_{39}KNO_{14}SSi_8$ 847.99, Found: 848.12 $(M{\cdot}K)^+$.

VPOSS-S-COOH (18). OctavinylPOSS (500 mg, 0.790 mmol), 2-mercaptoacetic acid **5** (73 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with CH_2Cl_2 as the eluent to afford the product as a white powder (143 mg, 25%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.16-5.87 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 3.29 (s, 2H, -C<u>H</u>$_2$COOH), 2.81 (t, 2H, -C<u>H</u>$_2$S-), 1.11 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 175.32, 137.06, 128.56, 33.10, 26.96, 12.46. MS (MALDI-TOF) (Figure S4): Calcd. for $C_{18}H_{28}NaO_{14}SSi_8$ 746.94, Found: 746.96 $(M{\cdot}Na)^+$; Calcd. *m/z* for $C_{18}H_{29}Na_2O_{14}SSi_8$ 768.91, Found: 768.94 $(M{\cdot}2Na\text{-}H)^+$.

VPOSS-S-Br (19). OctavinylPOSS (500 mg, 0.790 mmol), Br-SH **6** (179 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica

gel with hexanes/CH_2Cl_2 (v/v = 3/1) as the eluent to afford the product as a white powder (190 mg, 28%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.15-5.86 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 4.31 (t, 2H, -C<u>H</u>$_2$COO-), 2.80 (t, 2H, -SC<u>H</u>$_2$CH$_2$COO-), 2.72 (t, 2H, -SC<u>H</u>$_2$CH$_2$Si-), 1.95 (s, 6H, -CC$_2$<u>H</u>$_6$Br), 1.09 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 171.43, 137.04, 128.82, 65.03, 55.51, 30.79, 29.93, 26.47, 13.16. ^{28}Si NMR (40 MHz, $CDCl_3$, ppm, δ): -66.0, -75.1. MS (MALDI-TOF) (Figure 1d): Calcd. *m/z* for $C_{22}H_{35}BrNaO_{14}SSi_8$ 880.90, Found: 880.93 $(M{\cdot}Na)^+$.

VPOSS-S-N$_3$ (20). OctavinylPOSS (500 mg, 0.790 mmol), N_3-SH **7** (187 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 3/1) as the eluent to afford the product as a white powder (220 mg, 32%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.07 (d, 2H, -OCCC$_2$<u>H</u>$_2$-), 7.41 (d, 2H, -CH$_2$C$_2$<u>H</u>$_2$-), 6.15-5.85 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 4.46 (t, 2H, -C<u>H</u>$_2$COO-), 4.42 (s, 2H, -C<u>H</u>$_2$N$_3$), 2.90 (t, 2H, -SC<u>H</u>$_2$CH$_2$COO-), 2.74 (t, 2H, -SC<u>H</u>$_2$CH$_2$Si-), 1.12 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 187.34, 137.02, 130.18, 128.62, 127.94, 63.89, 54.27, 31.56, 30.32, 26.38, 13.24. MS (MALDI-TOF) (Figure S5): Calcd. *m/z* for $C_{26}H_{35}N_3NaO_{14}SSi_8$ 891.99, Found: 892.05 $(M{\cdot}Na)^+$.

VPOSS-S-AD (21). OctavinylPOSS (500 mg, 0.790 mmol), AD-SH **8** (258 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/3) as the eluent to afford the product as a white powder (198 mg, 26%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.15-5.86 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 4.23 (t, 2H, -SCH$_2$C<u>H</u>$_2$-), 3.70 (s, 2H, -COOC<u>H</u>$_2$C-), 2.77-2.61 (m, 8H, -C<u>H</u>$_2$SC<u>H</u>$_2$-+-OOCC$_2$<u>H</u>$_4$-), 1.98 [m, 3H, -C(CH$_2$C<u>H</u>)$_3$-], 1.74-1.47 [m, 12H, -C(C<u>H</u>$_2$CHC<u>H</u>$_2$-)$_3$], 1.08 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz,

$CDCl_3$, ppm, δ): 172.01,137.02, 128.64, 74.31, 63.58, 51.60, 39.24, 36.96, 33.19, 30.12, 29.13, 28.03, 26.32, 13.18. 13.24. MS (MALDI-TOF) (Figure S6): Calcd. *m/z* for $C_{33}H_{50}NaO_{16}SSi_8$ 981.09, Found: 981.18 $(M{\cdot}Na)^+$.

VPOSS-S-Fe (22). OctavinylPOSS (500 mg, 0.790 mmol), Fe-SH **9** (229 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 60 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with hexanes/CH_2Cl_2 (v/v = 1/8) as the eluent to afford the product as a red powder (146 mg, 20%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.15-5.86 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 4.81 (m, 2H, C_5H_2), 4.40 (m, 2H, C_5H_2), 4.36 (t, 2H, -CH_2C<u>H</u>$_2$COO-), 4.22 (s, 5H, C_5H_5), 2.86 (t, 2H, -C<u>H</u>$_2CH_2$COO-), 2.76 (t, 2H, -$SiCH_2C$<u>H</u>$_2$-), 1.13 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 172.12, 137.02, 128.62, 71.41, 70.74, 70.15, 69.84, 63.25, 29.75, 26.18, 11.25. MS (MALDI-TOF) (Figure S7): Calcd. *m/z* for $C_{29}H_{38}NaO_{14}SSi_8$ 921.96, Found: 922.07 $(M)^+$; Calcd. for $C_{29}H_{38}FeNaO_{14}SSi_8$ 944.94, Found: 945.06 $(M{\cdot}Na)^+$.

VPOSS-S-Sugar (23). OctavinylPOSS (500 mg, 0.790 mmol), Sugar-SH **10** (288 mg, 0.790 mmol), DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was then evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with EtoAc/CH_2Cl_2 (v/v = 1/2) as the eluent to afford the product as a white powder (181 mg, 23%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.16-5.86 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 5.26-4.99 (m, 3H, -C<u>H</u>OOC-), 4.53 (d, 1H,-SC<u>H</u>-), 4.26-4.11 (m, 2H, -C<u>H</u>$_2$OOC-), 3.71 (m, 1H, -C<u>H</u>CH_2OOC-), 2.81 (t, 2H, -SC<u>H</u>$_2$-), 2.03 (q, 12H, -OOCC<u>H</u>$_3$), 1.10 (t, 2H, -SiC<u>H</u>$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 170.23, 169.99, 169.19, 136.93, 128.44, 83.73, 69.81, 68.23, 63.56, 61.97, 29.52, 20.57,

13.23. MS (MALDI-TOF) (Figure S8): Calcd. *m/z* for $C_{30}H_{44}NaO_{21}SSi_8$ 1019.01, Found: 1019.07 $(M{\cdot}Na)^+$.

VPOSS-S-Dendron (24). OctavinylPOSS (500 mg, 0.790 mmol), Dendron-SH **11** (348 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with EtoAc/CH_2Cl_2 (v/v = 1/10) as the eluent to afford the product as a white powder (305 mg, 36%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 7.25 (s, 2H, Ar-H), 6.15-5.86 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 4.42 (t, 2H, -CH$_2$C<u>H</u>$_2$COO-), 4.02 (m, 6H,-C<u>H</u>$_2$OPh), 2.88 (t, 2H, -C<u>H</u>$_2$CH$_2$COO-), 2.73 (t, 2H, -SiCH$_2$C<u>H</u>$_2$-), 1.83 (m, 6H,-C<u>H</u>$_2$CH$_2$OPh), 1.45 (m, 12H, (-C$_2$<u>H</u>$_4$C$_2$H$_4$O-), 1.12 (t, 2H, -SiC<u>H</u>$_2$-), 0.94 (t, 9H, -CH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 166.14, 152.83, 142.58, 137.01, 128.62, 124.53, 108.15, 73.44, 69.19, 63.21, 29.95, 28.22, 22.40, 13.99, 13.20. MS (MALDI-TOF) (Figure S9): Calcd. *m/z* for $C_{40}H_{64}NaO_{17}SSi_8$ 1095.19, Found: 1095.31 $(M{\cdot}Na)^+$; Calcd. for $C_{40}H_{64}KO_{17}SSi_8$ 1111.17, Found: 1111.32 $(M{\cdot}K)^+$.

VPOSS-S-CONH-BPOSS (26). OctavinylPOSS (500 mg, 0.790 mmol), BPOSS-NHCO-SH **13** (817 mg, 0.790 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with EtoAc/CH_2Cl_2 (v/v = 1/10) as the eluent to afford the product as a white powder (539 mg, 41%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 6.15-5.85 (m, 21H, -C<u>H</u>=C<u>H</u>$_2$), 5.62 (s, 1H, -CON<u>H</u>-), 4.22 (t, 2H, -SCH$_2$C<u>H</u>$_2$-), 3.23 (m, 2H, -NHC<u>H</u>$_2$-), 2.78-2.66 (m, 6H, -C<u>H</u>$_2$SC<u>H</u>$_2$-+-C<u>H</u>$_2$CH$_2$COONH-), 2.46 (t, 2H, -C<u>H</u>$_2$COONH-), 1.86 (m, 7H, -SiCH$_2$C<u>H</u>C$_2$H$_6$), 1.59 (m, 2H, -NHCH$_2$C<u>H</u>$_2$-), 1.08-0.95 (m, 44H, -SiC<u>H</u>$_2$CH$_2$S-+-SiCH$_2$CHC$_2$<u>H</u>$_6$), 0.60 (q, 16H, -SiC<u>H</u>$_2$CH-+-SiC<u>H</u>$_2$CH$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 171.67, 170.92, 136.99, 128.62,

63.50, 41.91, 31.01, 30.17, 29.50, 26.31, 25.67, 23.87, 23.82, 22.49, 9.44. MS (MALDI-TOF) (Figure S10): Calcd. *m/z* for $C_{53}H_{103}NNaO_{27}SSi_{16}$ 1688.26, Found: 1688.30 $(M{\cdot}Na)^+$.

VPOSS-(S-BPOSS)$_2$. Octavinyl POSS (500 mg, 0.790 mmol), BPOSS-SH **12** (1408 mg, 1.580 mmol), and DMPA (4 mg, 0.0158 mmol) were dissolved in 50 mL of THF. After irradiation for 30 min, THF was evaporated under vacuum. Then the crude product VPOSS-(S-BPOSS)$_2$ was analyzed by ESI-TWIM MS without purification.

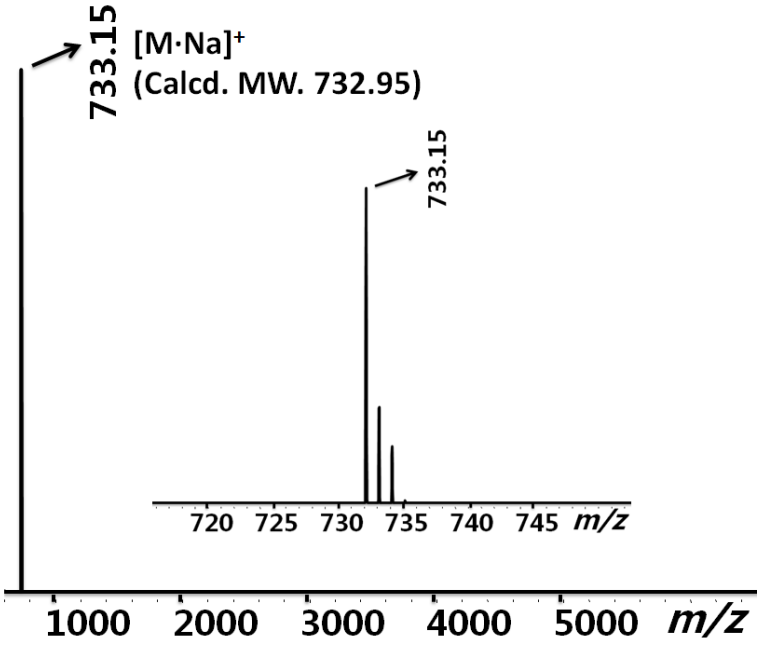


Figure S1. MALDI-TOF mass spectrum of VPOSS-S-OH **14**; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

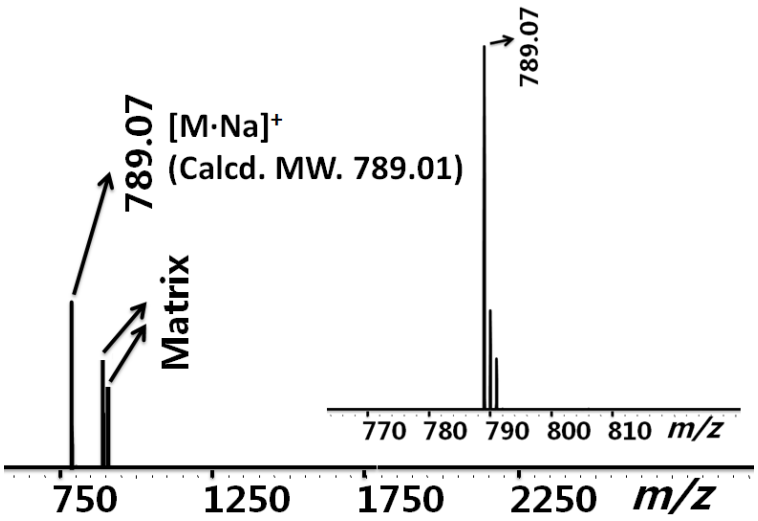


Figure S2. MALDI-TOF mass spectrum of VPOSS-S-C_6-OH **15**; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

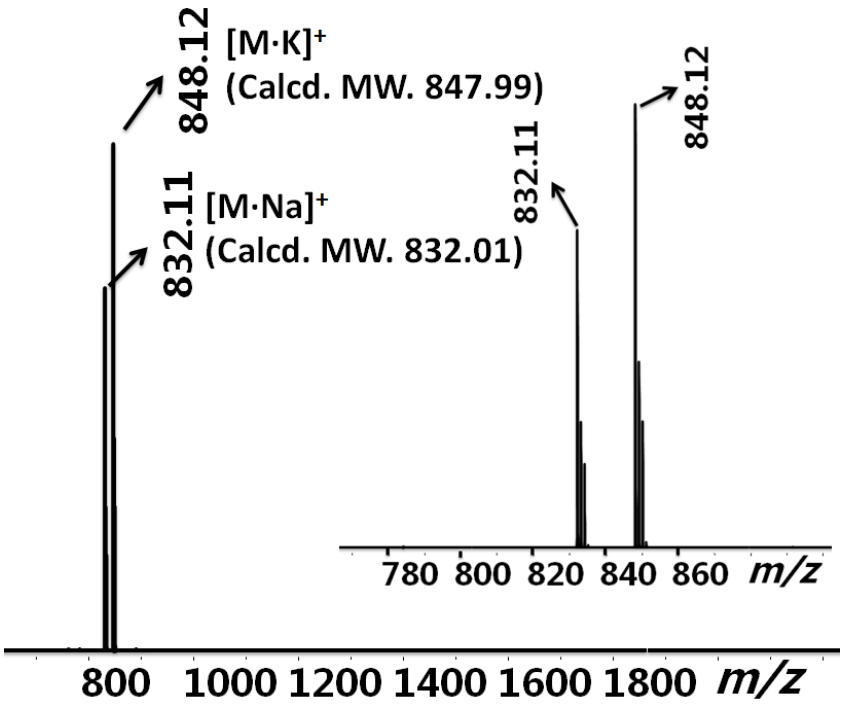


Figure S3. MALDI-TOF mass spectrum of VPOSS-S-NH-Boc **17**; the zoom-in view provided in the inset shows the isotope patterns of the $[M{\cdot}Na]^+$ and $[M{\cdot}K]^+$ ions.

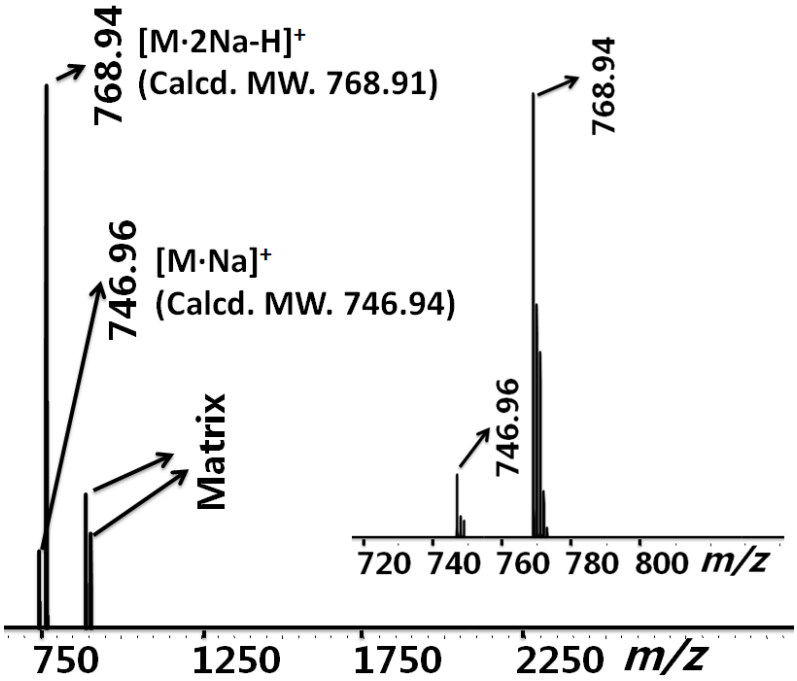


Figure S4. MALDI-TOF mass spectrum of VPOSS-S-COOH **18**; the zoom-in view provided in the inset shows the isotope patterns of the $[M{\cdot}2Na\text{-}H]^+$ and $[M{\cdot}Na]^+$ ions.

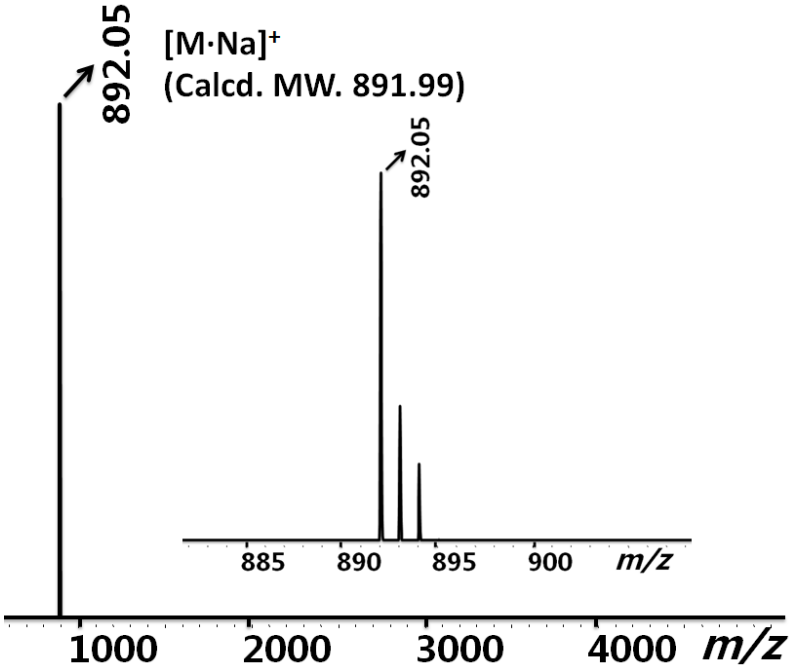


Figure S5. MALDI-TOF mass spectrum of VPOSS-S-N_3 **20**; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

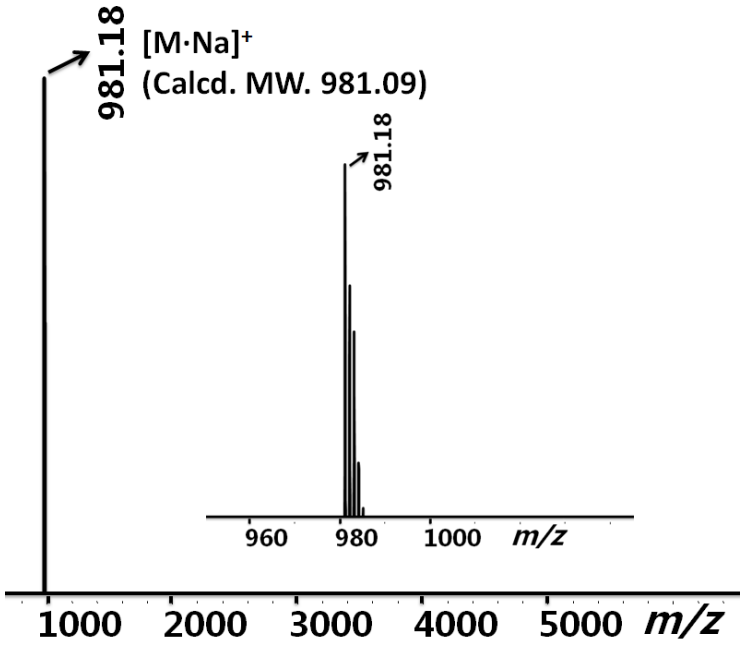


Figure S6. MALDI-TOF mass spectrum of VPOSS-S-AD **21**; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

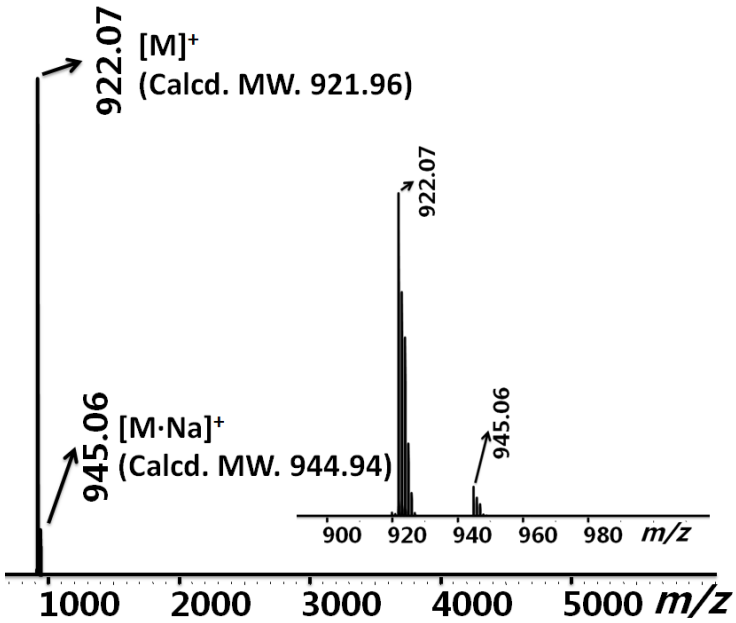


Figure S7. MALDI-TOF mass spectrum of VPOSS-S-Fe **22**; the zoom-in view provided in the inset shows the isotope patterns of the $[M]^+$ and $[M{\cdot}Na]^+$ ions.

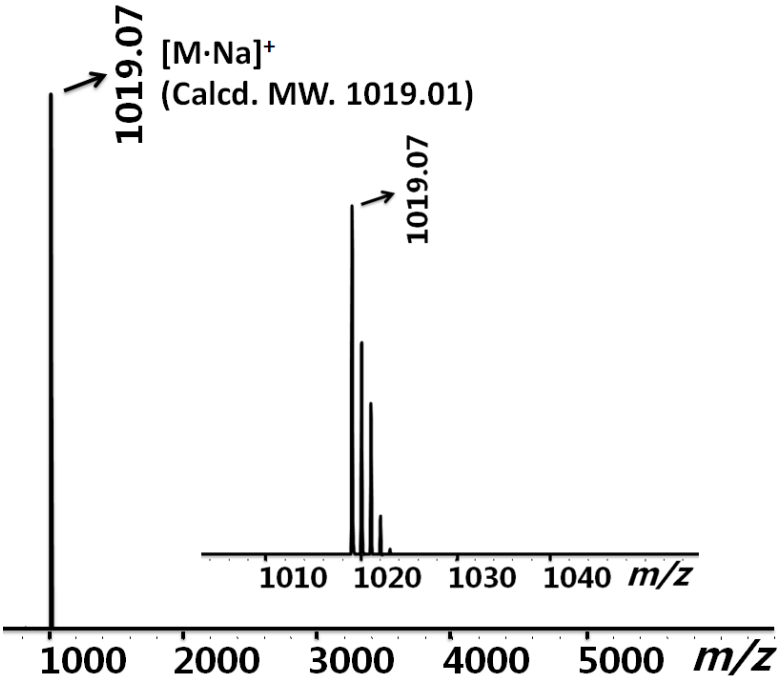


Figure S8. MALDI-TOF mass spectrum of VPOSS-S-Sugar **23**; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

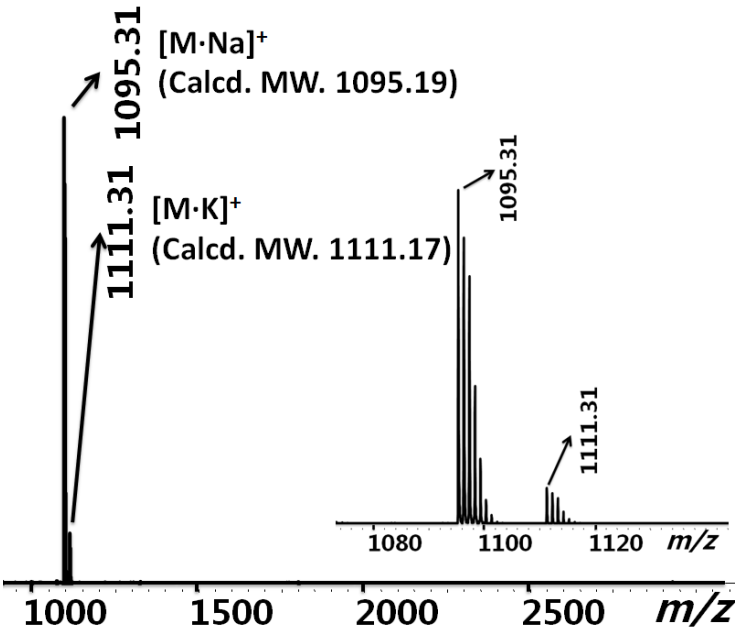


Figure S9. MALDI-TOF mass spectrum of VPOSS-S-Dendron **24**; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ and $[M{\cdot}K]^+$ ions.

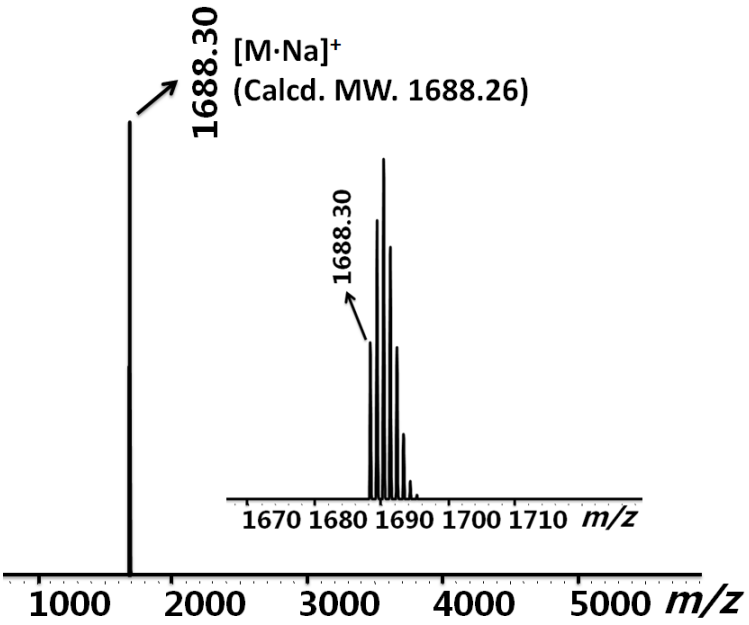


Figure S10. MALDI-TOF mass spectrum of VPOSS-S-CONH-BPOSS **26**; the zoom-in view rovided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

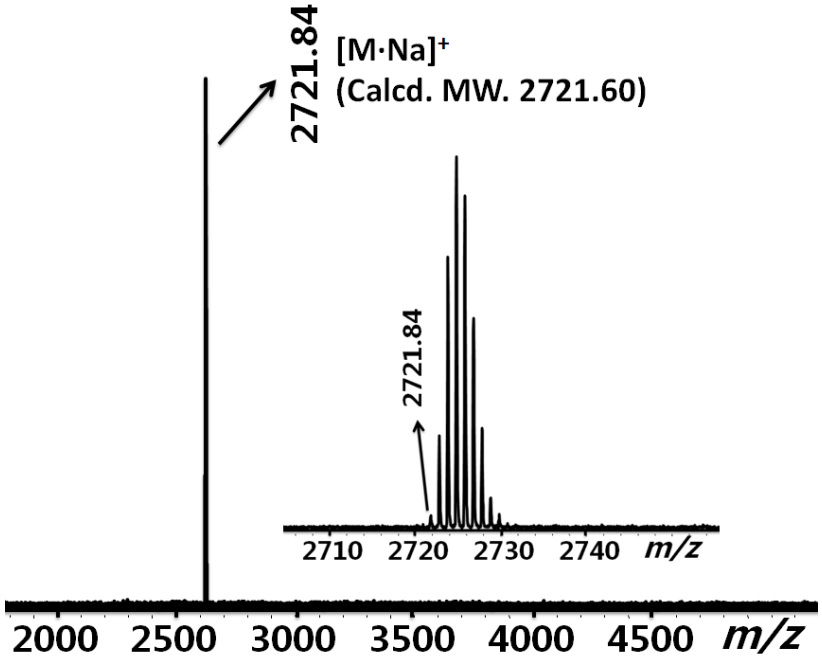


Figure S11. MALDI-TOF mass spectrum of VPOSS-(S-CONH-BPOSS)$_2$; the zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion.

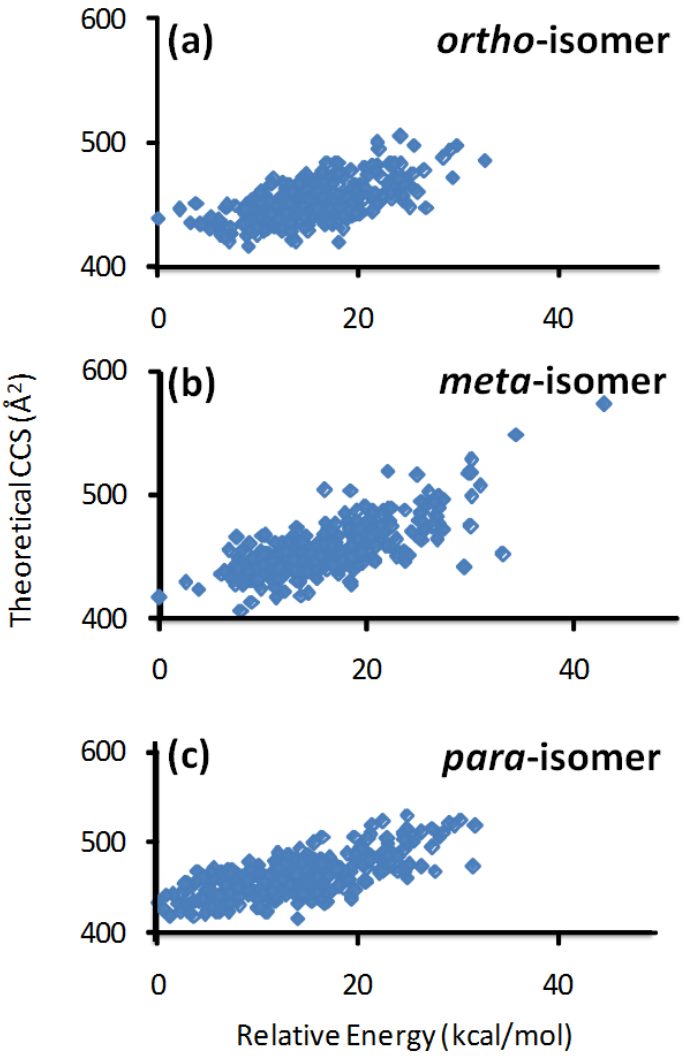


Figure S12. Calculated collision cross-sections *vs.* the corresponding relative energies for the energy-minimized structures of the three different oxidized VPOSS-(S-BPOSS)$_2$ isomers.

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