Supplementary Information for:

Spherosilicates with Peripheral Malonic Acid and Vinyl End Groups

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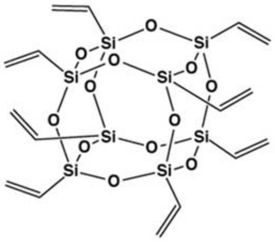
I. Experimental Procedures

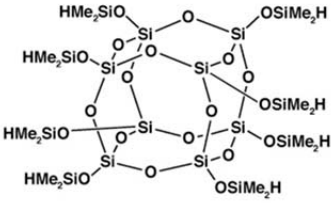
General Procedures. Dry tetrahydrofuran, diethyl ether, toluene, and toluene-d_8 were distilled from sodium/benzophenone ketyl. All other solvents (anhydrous), reagents and catalysts were purchased commercially and were used without further purification. Allylmalonic acid (99%, Alfa Aesar), benzyl alcohol (99%, Sigma-Aldrich), $[Si_8O_{12}]$-$(OSiMe_2H)_8$ (95%, Sigma-Aldrich), diethylamine (99%, Sigma-Aldrich), 1,4-bis-dimethylsilylbenzene (97%, ABCR). The Karstedt catalyst (a platinum(0) divinyl tetramethyldisiloxane complex in xylene, 2.1~2.4 wt% Pt, Gelest Inc) was used for hydrosilylation. Pt/C (30 wt%, Sigma-Aldrich) was used for the hydrogenolysis. Smopex-301 (Alfa Aesar) was used to scavenge Pt(0) after hydrosilylation reaction to from **VI**. Thin layer chromatography was performed on silica gel plates Merck 60 F_{254}. The compounds were detected by UV. Dibenzyl allylmalonate **I** and $[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOBz)_2)_8$ **III** were purified by silica gel column chromatography (pore size 60Å, 70-230 mesh, Sigma-Aldich). Experiments involving $[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8$ **IV** and $[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOSi(CH{=}CH_2)_3)_2)_8$ **V** were performed using dry box or Schlenk techniques under a nitrogen atmosphere.

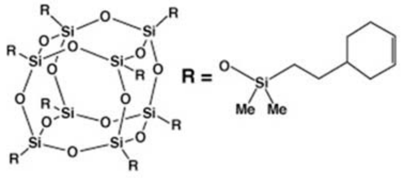
Analytical Methods. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded with a Varian INOVA 400 spectrometer, operated at 400 MHz for ^1H, 100 MHz for ^{13}C and 79 MHz for ^{29}Si. NMR spectra of the moisture sensitive compound **V** were recorded in sealed J. Young NMR tubes. The ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H solvent resonances. The ^{29}Si NMR chemical shift was referenced to TMS at 0.0 ppm. The chemical shifts reported are in ppm and coupling constants in Hz. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) of **III** was recorded on a PerSeptive Biosystems Voyager DE-STR spectrometer operated in a linear mode with positive polarity. 2-hydroxy-1-naphthoic acid was used as the matrix. Electron Spray Mass spectrometry (ESI-MS) spectra of **III** and **V** were recorded on the Applied Biosystems API3000 spectrometer. Powder X-ray diffraction of **III** (XRD, Scintag XDS2000, Cu-Kα radiation ($\lambda = 1.5418$ Å) was run at 40 kV, scan range $2\theta = 5^o - 90^o$, and step rate = 0.05^o/s. Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN). Small angle X-ray scattering of **VI** (in toluene solution at different concentrations as mentioned in the text) was measured at APS of Argonne

National Laboratory. Dynamic light scattering of **VI** (in toluene solution at 1 mg/mL) was measured using Malvern Zetasizer Nano S, and refractive index of polystyrene (1.57) was used. Gel permeation chromatography of **VI** was performed on a Waters Breeze instrument using THF as the eluent and six $[Si_8O_{12}]$-R_8 (Chart S1, MW = 600 – 6000) as calibration standards.

Chart S1. Standards used for GPC molecular weight calibration







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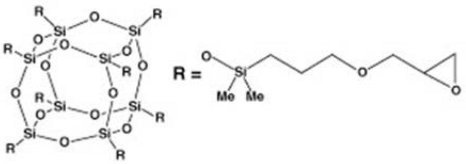

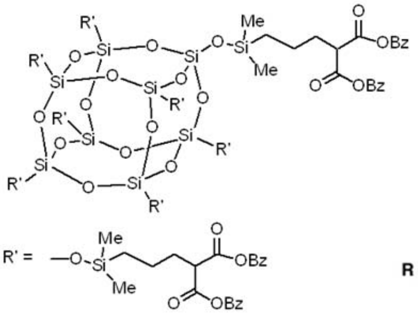

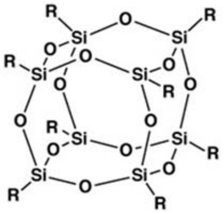

$R = -CH_2CH_2(OCH_2CH_2)_mOCH_3$, m = ~13.3

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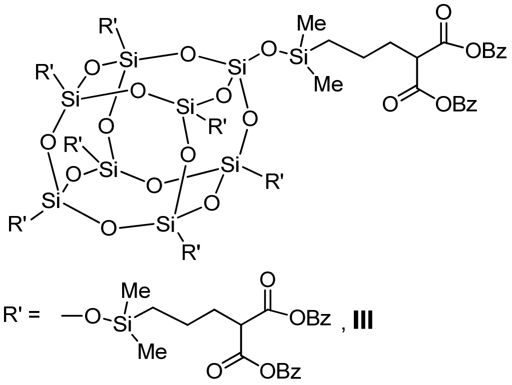
II. Synthesis and Characterization of Compounds.

Dibenzyl Allylmalonate I. Into a flask loaded with allylmalonic acid (4.32 g, 30 mmol), benzyl alcohol (7.46 mL, 70 mmol) and anhydrous toluene (30 mL), H_2SO_4 (95.8%, 0.030 mL) was added dropwise under stirring. The solution was refluxed for 2 h with a Dean-Stark apparatus to remove water. The reaction was monitored with thin-layer chromatography (TLC). When the allylmalonic acid disappeared, the solution was cooled down and washed by saturated sodium bicarbonate solution, sodium chloride solution and distilled water. The desired compound, dibenzyl allylmalonate, was purified by column chromatography (eluent: hexane/ethyl acetate = 9/1 by volume). Yield: 4.10 g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.68 (t, 2H, *J* = 7); 3.55 (t, 1H, *J* = 7); 5.03 (d, 1H, *J* = 10); 5.08 (d, 1H, *J* = 17); 5.14 (m, 4H); 5.76 (m, 1H); 7.19 – 7.39 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.95; 51.79; 67.30; 117.93; 128.34; 128.49; 128.68; 133.93; 135.44; 168.74. Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.25; H, 6.05.

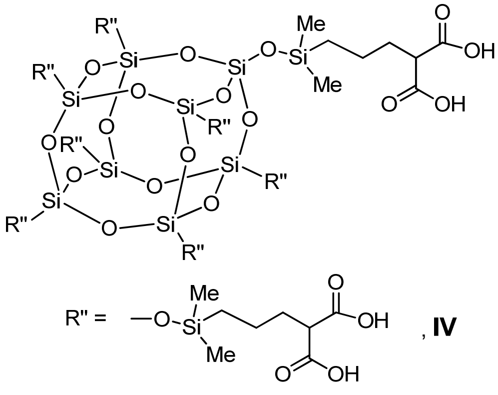


$[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOBz)_2)_8$

$[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOBz)_2)_8$ III. A flame dried 150 ml two-neck flask was loaded with $[Si_8O_{12}]$-$(OSiMe_2H)_8$ (0.893 g, 0.877 mmol), dibenzyl allylmalonate (2.60 g, 8.77

mmol) and anhydrous THF (40 mL). The solution was heated to 40 °C. Karstedt′s catalyst (platinum divinyltetramethyldisiloxane [Pt(dvs)], 20 mL) was added to the solution to catalyze the hydrosilylation reaction. The reaction was monitored by ^{1}H NMR for the disappearance of the Si-H signal. The solution was stirred for 6 h at 40 °C to reach completion. The product was purified by column chromatography. Unreacted dibenzyl allylmalonate was first removed using hexane/ethyl acetate = 4/1 by volume). The eluent was then changed to hexane/ethyl acetate = 3/1 by volume to purify **III**. Yield: 2.58 g (87%). The product was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and MALDI-tof.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.044 (s, 48H); 0.55 (t, 16H, *J* = 8); 1.29 (m, 16H); 1.92 (q, 16H, *J* = 7); 3.43 (t, 8H, *J* = 8); 5.17 (m, 32H); 7.14 – 7.38 (m, 80H). ^{13}C NMR (CDCl3, 100 MHz): δ -0.096; 17.58; 21.17; 32.53; 51.99; 67.28; 128.46; 128.60; 128.85; 135.80; 169.44. ^{29}Si NMR (CDCl$_3$, 79 MHz): δ -112.9; 8.64. MALDI (*m/z*, DHB matrix): 3632 (90%, M + Na$^+$), 3648 (100%, M + K$^+$). Anal. Calcd. for $C_{176}H_{216}O_{52}Si_{16}$: C, 58.51; H, 6.03. Found: C, 58.44; H, 6.09.



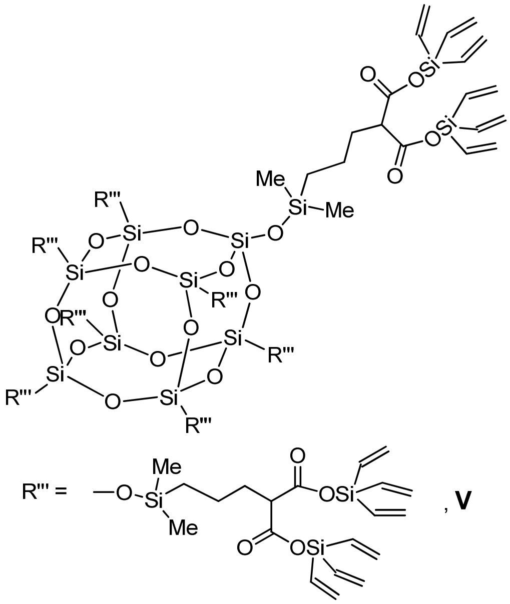
, **IV**

$[Si_8O_{12}]\text{-}(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8$

$[Si_8O_{12}]\text{-}(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8$ IV. Into a flask loaded with **III** (2.58 g) and

Pd/C catalyst (30 wt%, 10 mg), a mixed solvent MeOH/THF (1/9 by volume, 40 mL) was added under N_2. H_2 gas was constantly bubbled into the solution for 7 h under stirring at room temperature. The mixture was then filtered through a PTFE membrane syringe filter (dia. 0.45 μm) to remove the catalyst. The volatiles of the resulting clear filtrate were removed under vacuum to yield a colorless oil. The oil was evacuated under high vacuum for overnight to afford a white solid. Yield: 1.50 g (97%). The product was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.

^{1}H NMR (THF-d_8, 400 MHz): δ 0.13 (s, 48H); 0.64 (t, 16H, $J = 8$); 1.38 (m, 16H); 1.82 (q, 16H, $J = 8$); 3.22 (t, 8H, $J = 8$). ^{1}H NMR (dry DMSO-d_6, 400 MHz): δ 0.10 (s, 48H); 0.59 (t, 16H, $J = 8$); 1.31 (m, 16H); 1.72 (q, 16H, $J = 8$); 3.22 (t, 8H, $J = 8$); 12.6 (s, 16H). ^{13}C NMR (THF-d_8, 100 MHz): δ 0.51; 18.75; 22.46; 33.88; 52.48; 171.74. ^{29}Si NMR (THF-d_8, 79 MHz): δ -103.35; 18.36. ESI-MS (THF, negative ion scan, *m/z*): 1084 $(M - 2H^+)^{2-}$. Anal. Calcd. for $C_{64}H_{120}O_{52}Si_{16}$: C, 35.41; H, 5.57. Found: C, 35.25; H, 5.65.



, **V**

$[Si_8O_{12}]\text{-}(OSiMe_2CH_2CH_2CH_2CH(COOSi(CH{=}CH_2)_3)_2)_8$

[Si_8O_{12}]-($OSiMe_2CH_2CH_2CH_2CH(COOSi(CH{=}CH_2)_3)_2)_8$ V. A Schlenk flask was loaded with [Si_8O_{12}]-($OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8$ (**IV**, 1.01 g, 0.465 mmol), trivinylchlorosilane (1.38 mL, 8.91 mmol) and Et_2O (50 mL). Diethylamine (0.92 mL, 8.95 mmol) was added dropwise under N_2 and vigorous stirring. Lots of white precipitate (Et_2NH_2Cl) formed. The mixture was stirred for 20 min. The product was obtained by cannula filtration, followed by the removal of the volatiles. Yield: 1.54 g (85%). This compound is highly moisture sensitive.

^{1}H NMR (toluene-d_8, 400 MHz): δ 0.26 (s, 6H); 0.66 (t, 2H, *J* = 8); 1.46 (m, 2H); 2.01 (q, 2H, *J* = 8); 3.40 (t, 1H, *J* = 8); 5.94 - 6.33 (two groups of multiplets, 18H). ^{13}C NMR (toluene-d_8, 100 MHz): δ -0.11; 17.65; 21.09; 32.64; 54.52; 132.05; 137.24, 168.94. ^{29}Si NMR (toluene-d_8, 79 MHz): δ -107.86; -14.70, 13.52. ESI-MS (CH_2Cl_2, positive ion scan, *m/z*): 1969.5 ($(M + 2NH_4^+)^{2+}$).

Core-Shell Nanosphere VI. A 500 mL Schlenk flask was loaded with [Si_8O_{12}]-($OSiMe_2CH_2CH_2CH_2CH(COOSi(CH{=}CH_2)_3)_2)_8$ (**V**, 390 mg, 0.100 mmol), Karstedt catalyst (0.05 mL) and toluene (300 mL). The solution was heated to 100 °C under vigorous stirring and N_2. A solution of 1,4-bis-dimethylsilylbenzene (419 mg, 2.16 mmol) in toluene (20 mL) was added over a period of 20 hours with the aid of a syringe pump. A yellow solution formed. The solution was treated with 100 mg Smopex-301at 80 °C for 4 hours to remove Pt(0). The resulting solution after filtration was colorless, and was diluted for DLS and SAXS analyses. The volatiles were removed under vacuum, and the resulting pale yellow oil was dissolved in THF for GPC and toluene-d_8 for NMR.

^{1}H NMR (toluene-d_8, 400 MHz): δ 0.3 - 1.3 (broad overlapped, 26H); 3.5 (very broad); 6.1 (br, 1.0H); 7.6 (br, 4.2H). ^{29}Si NMR (toluene-d_8, 79 MHz): δ -103.5; 3.4; 17.7; 29.9, and all peaks are broad.

III. NMR, MS and IR Spectra of Key compounds.

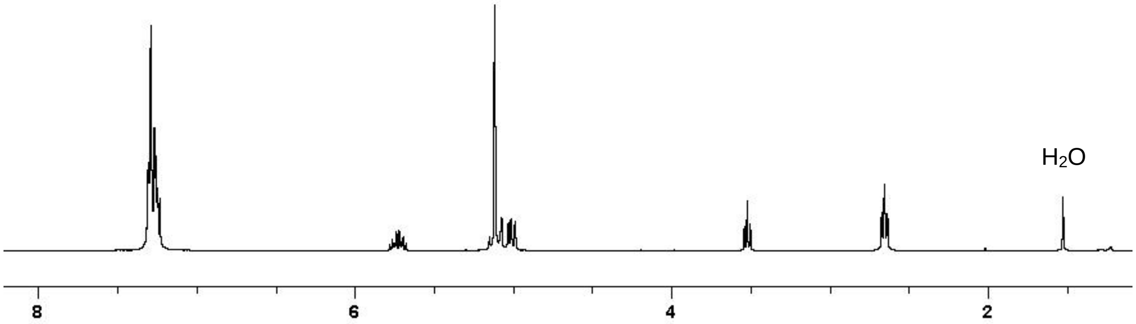


Fig. S1 ^{1}H NMR spectrum of dibenzyl allylmalonate **I**.

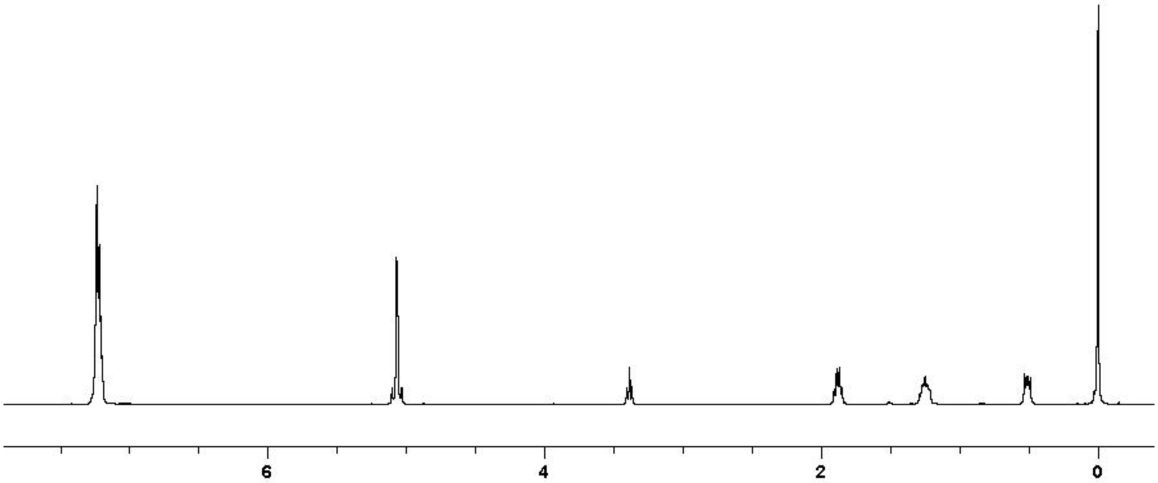


Fig. S2a ^{1}H NMR spectrum of $[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOBz)_2)_8$ **III** in $CDCl_3$.

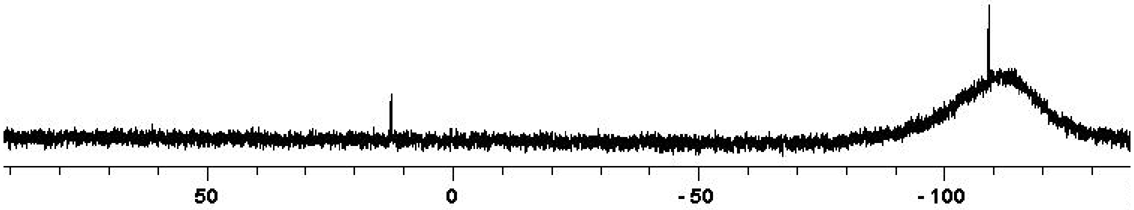


Fig. S2b ^{29}Si NMR spectrum of **III** in $CDCl_3$.

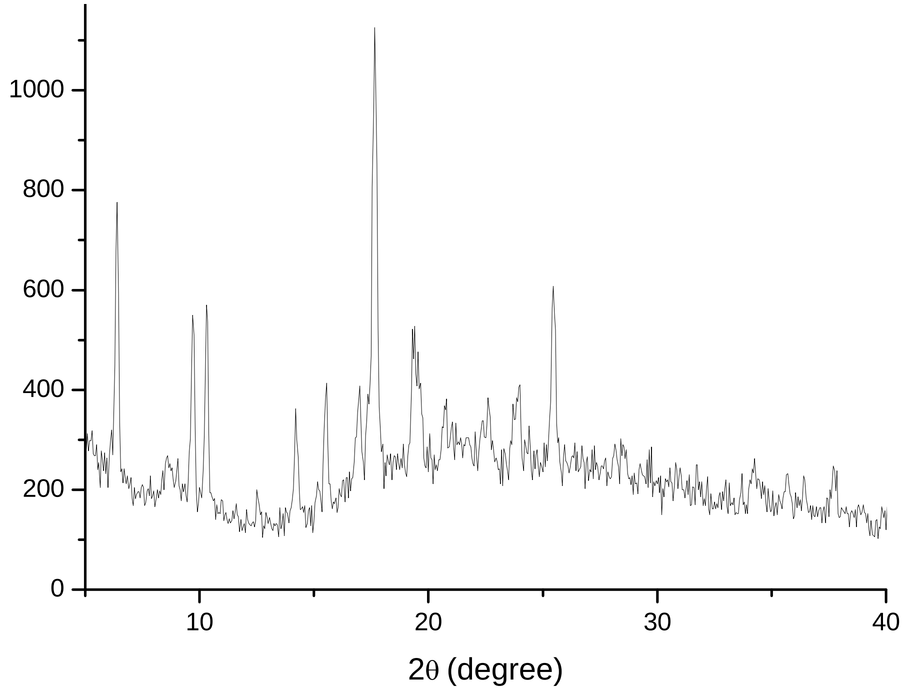


Fig. S3a Powder XRD spectrum of $[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8$ **IV**.

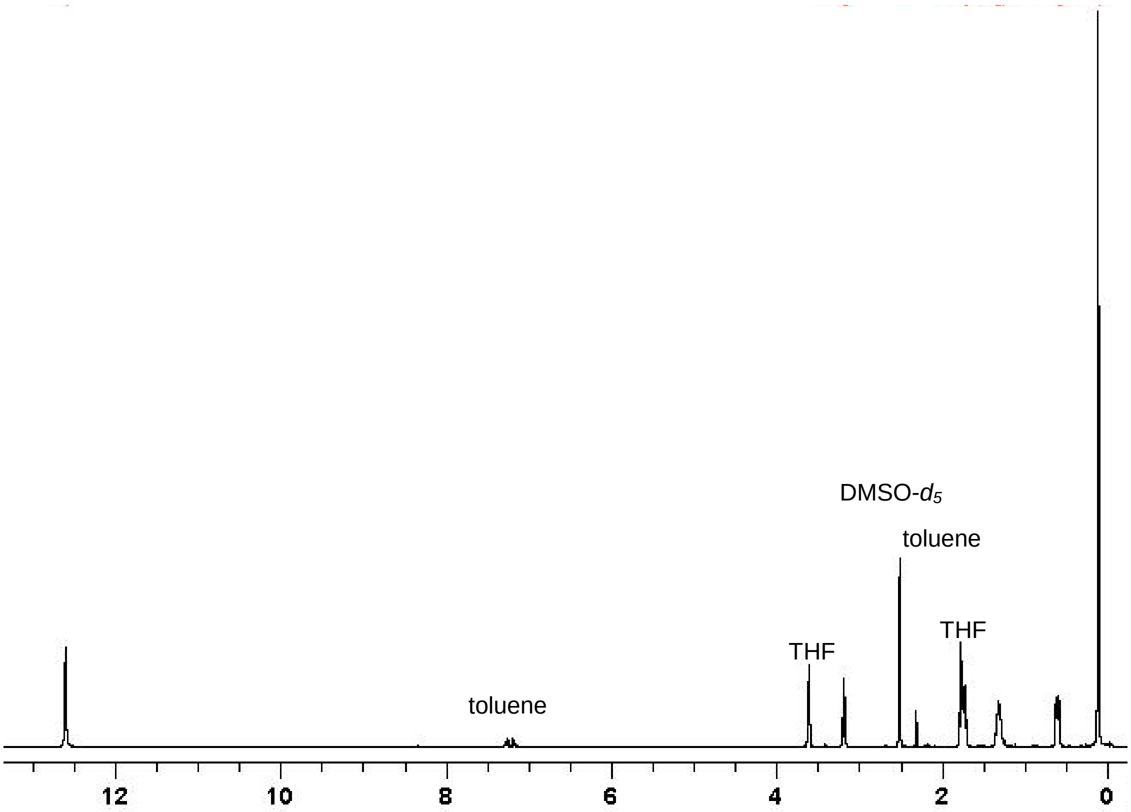


Fig. S3b ^1H NMR spectrum of $[Si_8O_{12}]$-$(OSiMe_2CH_2CH_2CH_2CH(COOH)_2)_8$ **IV** in dry

DMSO-d_6.

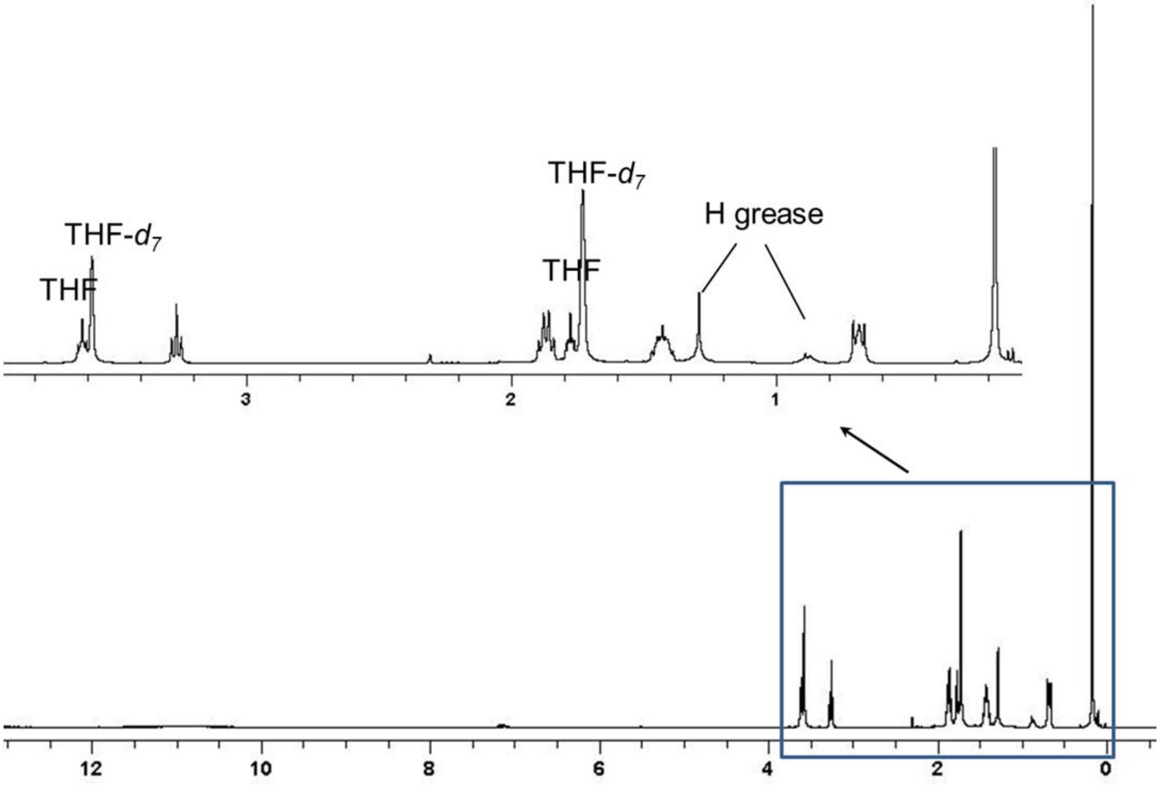


Fig. S3c ^{1}H NMR spectrum of **IV** (a different batch from Fig. S3b) in wet THF-d_8.

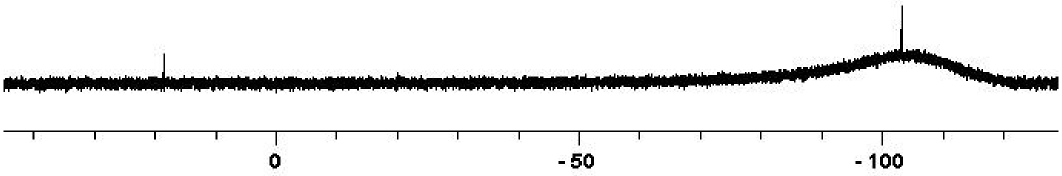


Fig. S3d ^{29}Si NMR spectrum of **IV** (same batch as for Fig. S-3b) in wet THF-d_8.

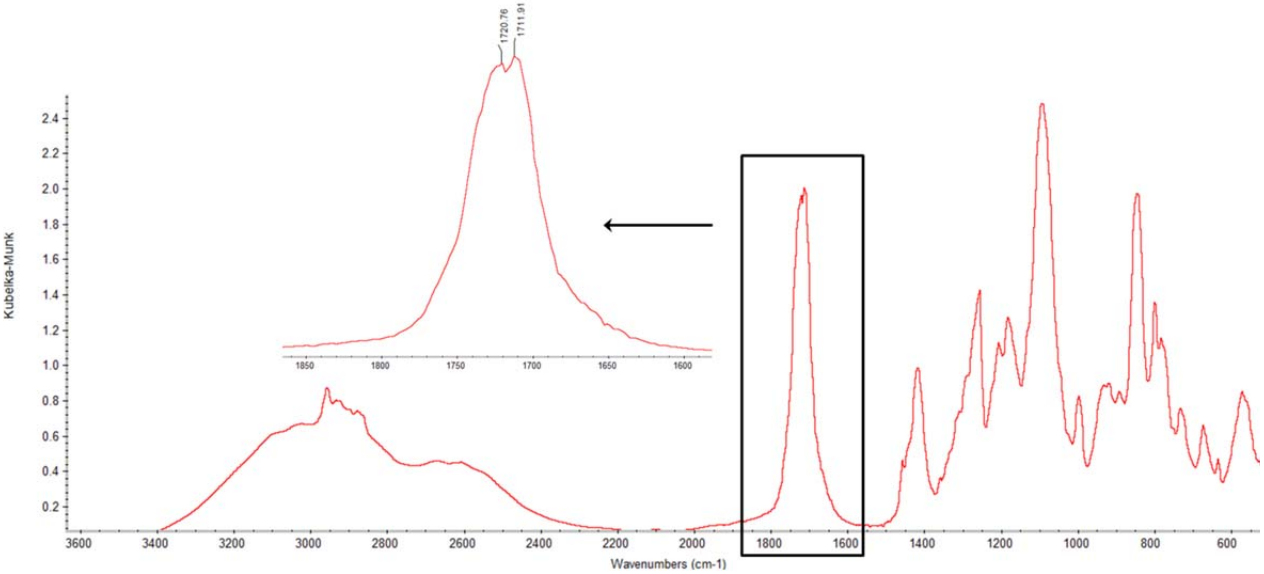


Fig. S3e FT-IR spectrum of **IV**.

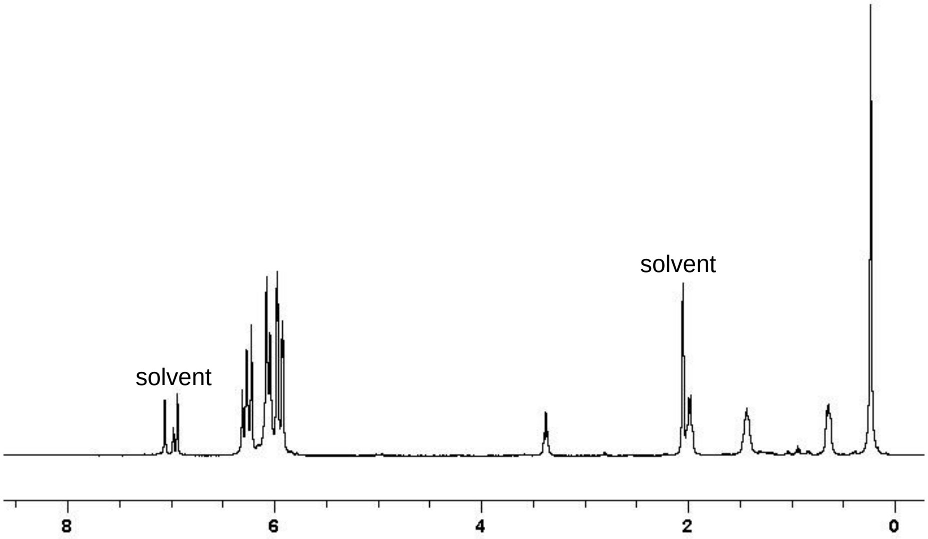


Fig. S4a ^{1}H NMR spectrum of [Si$_8$O$_{12}$]-(OSiMe$_2$CH$_2$CH$_2$CH$_2$CH(COOSi(CH=CH$_2$)$_3$)$_2$)$_8$ **V** in dry toluene-*d*$_8$.

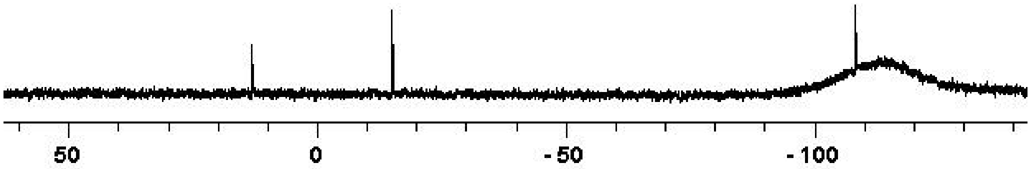
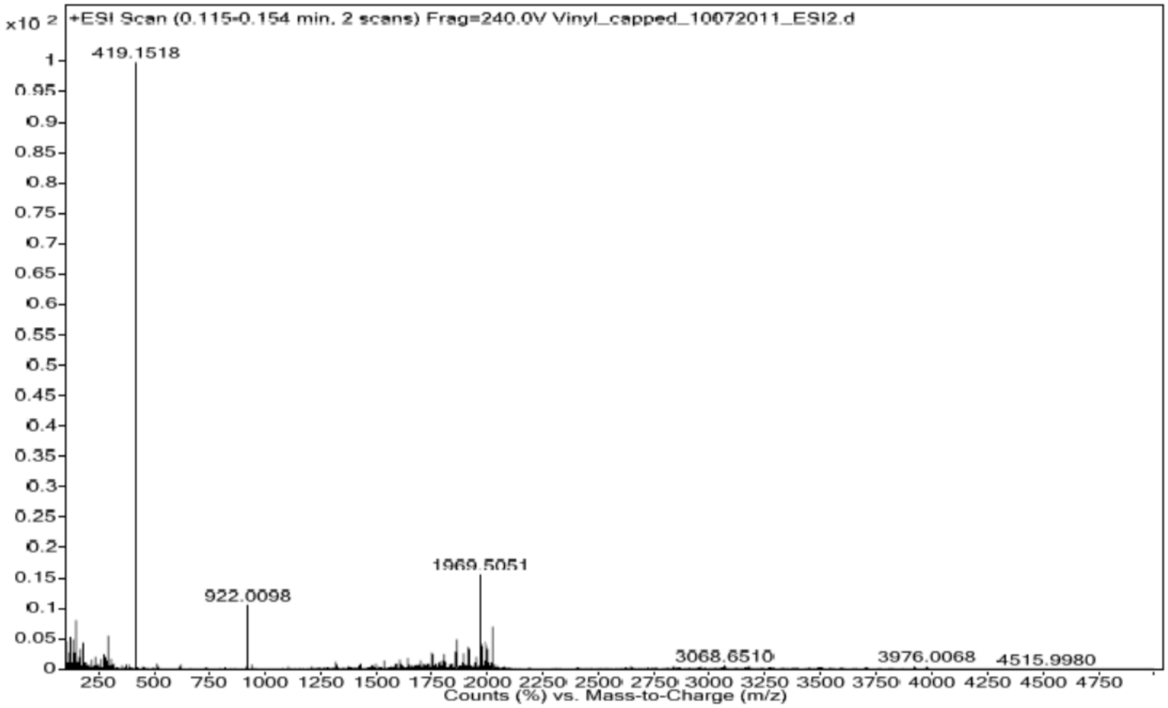
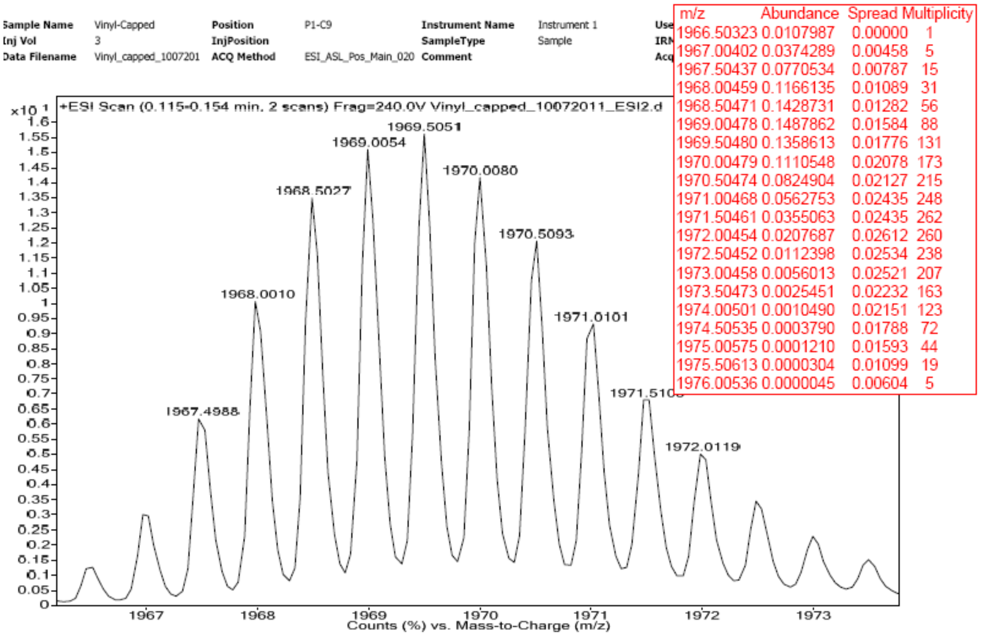


Fig. S4b ^{29}Si NMR spectrum of **V** in dry toluene-*d*$_8$.





Sample Name	Vinyl-Capped	**Position**	P1-C9	**Instrument Name**	Instrument 1	**Use**
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRN**
Data Filename	Vinyl_capped_1007201	**ACQ Method**	ESI_ASL_Pos_Main_020	**Comment**		**Acq**

m/z	Abundance	Spread	Multiplicity
1966.50323	0.0107987	0.00000	1
1967.00402	0.0374289	0.00458	5
1967.50437	0.0770534	0.00787	15
1968.00459	0.1166135	0.01089	31
1968.50471	0.1428731	0.01282	56
1969.00478	0.1487862	0.01584	88
1969.50480	0.1358613	0.01776	131
1970.00479	0.1110548	0.02078	173
1970.50474	0.0824904	0.02127	215
1971.00468	0.0562753	0.02435	248
1971.50461	0.0355063	0.02435	262
1972.00454	0.0207687	0.02612	260
1972.50452	0.0112398	0.02534	238
1973.00458	0.0056013	0.02521	207
1973.50473	0.0025451	0.02232	163
1974.00501	0.0010490	0.02151	123
1974.50535	0.0003790	0.01788	72
1975.00575	0.0001210	0.01593	44
1975.50613	0.0000304	0.01099	19
1976.00536	0.0000045	0.00604	5

Fig. S5 ESI-MS (positive ion scan) of **V**, showing the region up to *m/z* = 5000 (top); the expansion of the signal peaked at *m/z* = 1969.5051, numbers in red show the theoretical *m/z* distributions for (**V** + 2 NH_4^+)$^{2+}$ (bottom).

IV. Thermo Stability of Compound V

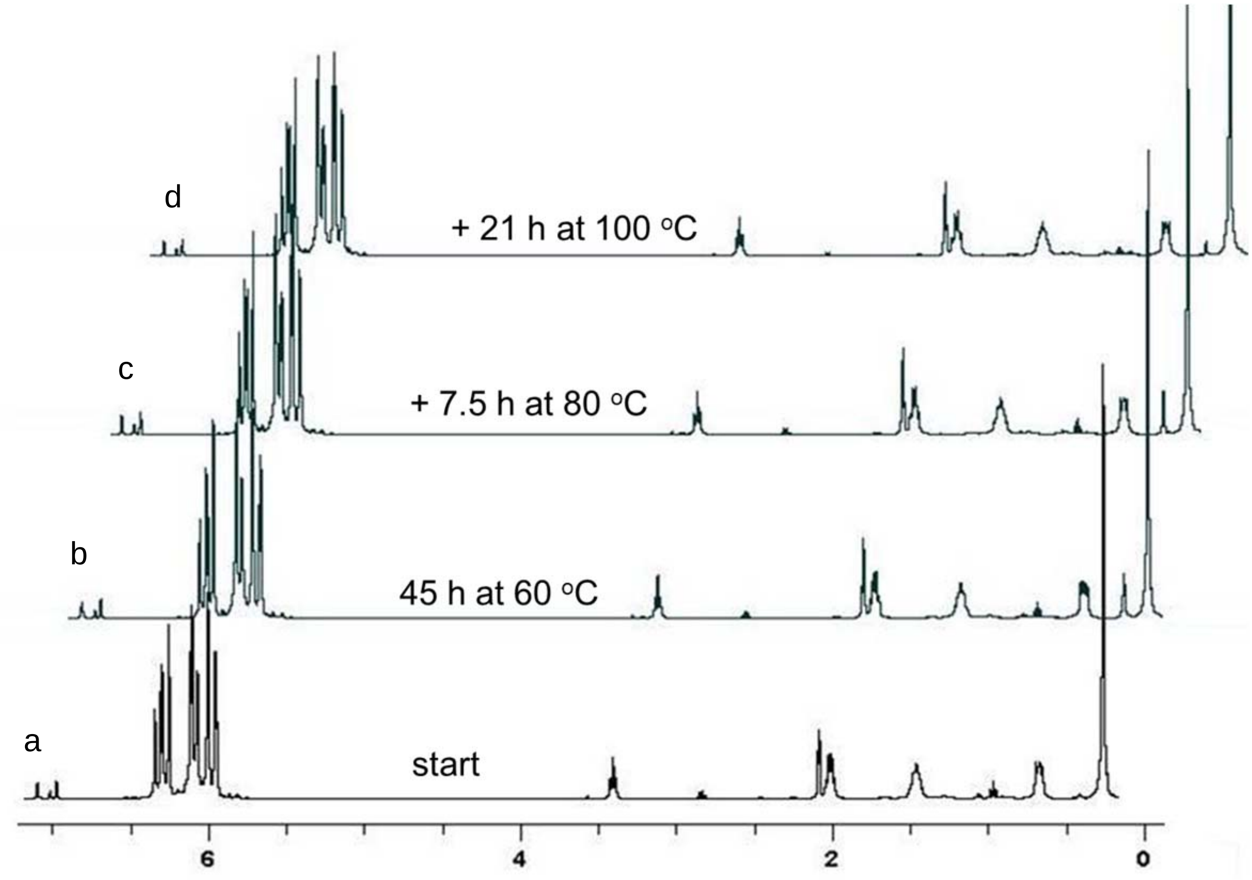


Fig. S6 ^{1}H NMR spectra of (a) starting material **V** in dry toluene-d_8; (b) sample a after heating at 60 °C for 45 h; (c) sample b after further heating at 80 °C for 7.5 h; (d) sample c after further heating at 100 °C for 23 h.

V. NMR, DLS, SAXS, and GPC characterization of nanosphere VI

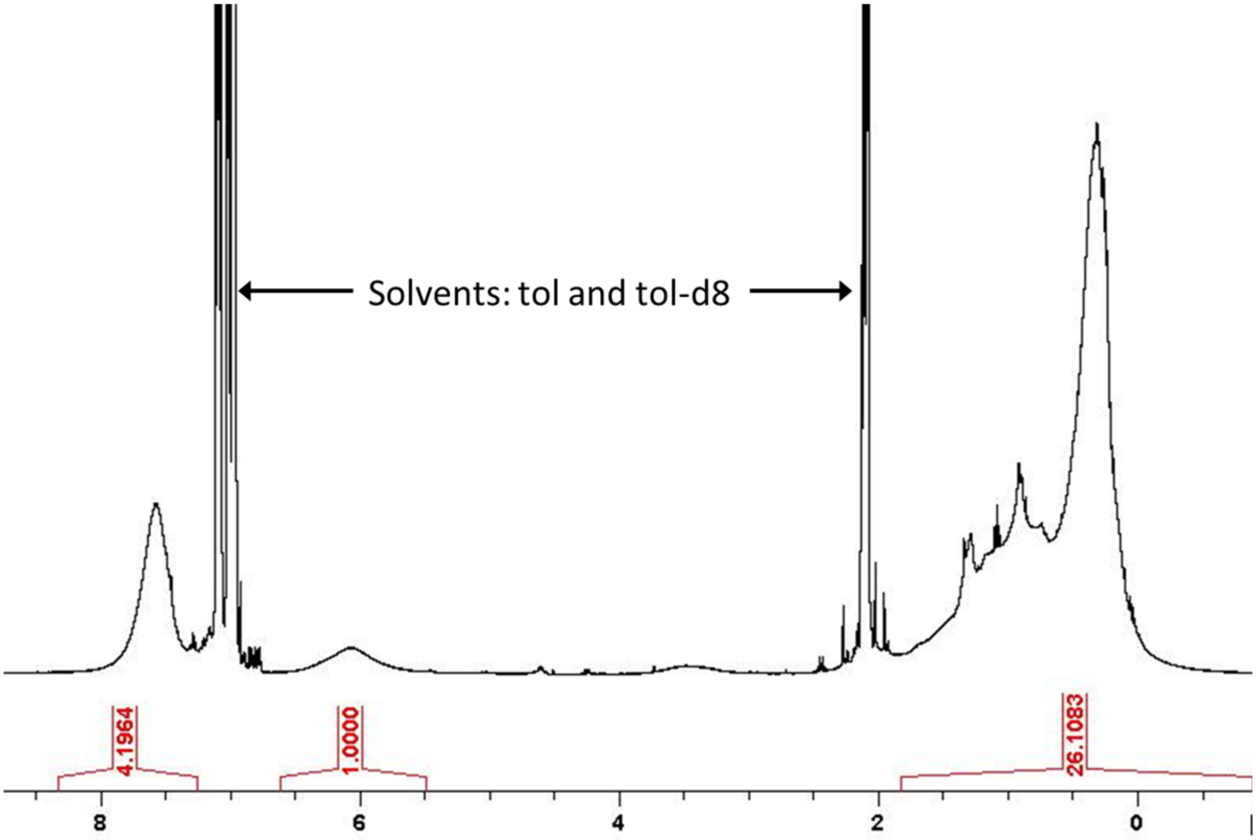


Fig. S7a ^{1}H NMR spectrum of nanosphere **VI** in toluene-d8**.**

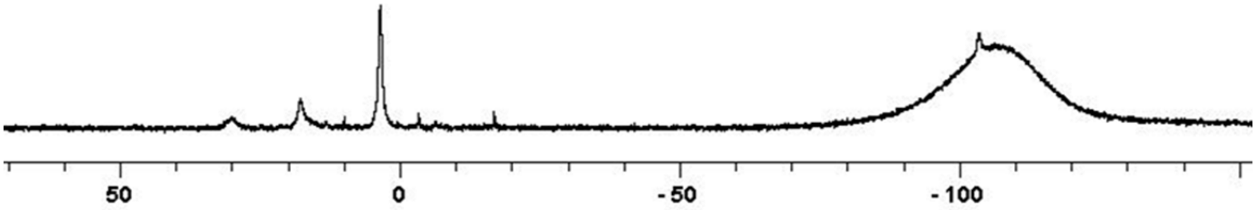


Fig. S7b ^{29}Si NMR spectrum of nanosphere **VI** in toluene-d8**.**

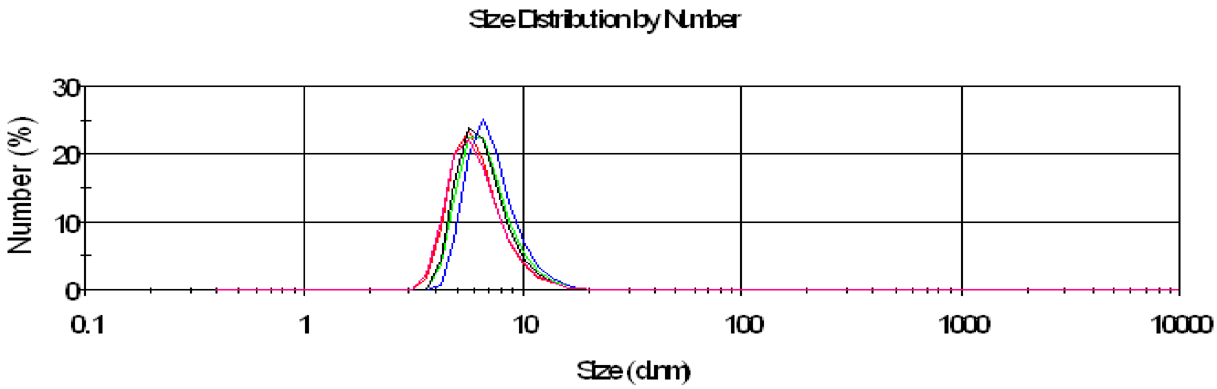


Fig. S8 DLS results of hydrodynamic size distribution of **VI** in toluene. Different curves stand for different runs. The results are consistently in the range of 6.4 and 7.4 nm.

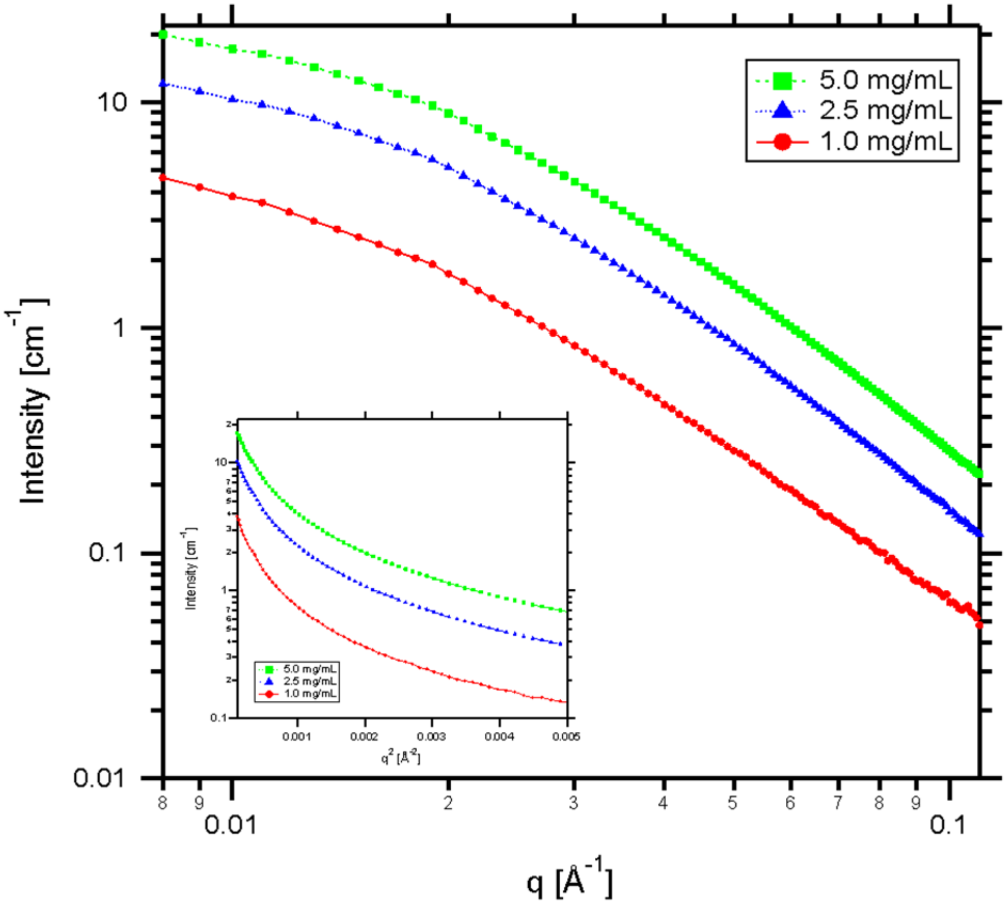
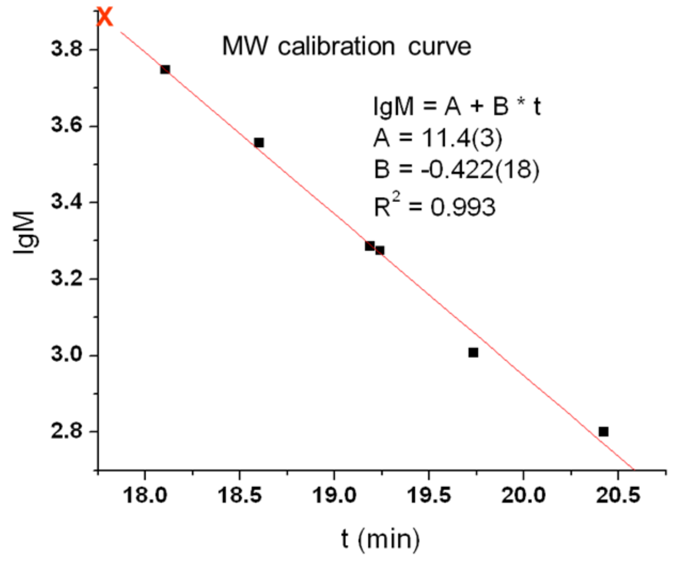


Fig. S9 SAXS results of **VI** in toluene. Radius of gyration: 2.1 nm at 1.0 mg/mL, 4.9 nm at 2.5 mg/mL, and 5.0 nm at 5.0 mg/mL. These results suggested aggregation at concentrations higher than 2.5 mg/mL. Inset shows the Guinier plot of the SAXS data.



Elution time of **VI**: 17.767 min → MW = 7,900

Theoretical MW for a 86% shell cross-linked nanosphere: 7,900

Fig. S10 GPC calibration curve and estimated MW of **VI** based on the retention time. Experimental results (7,900) agree with theoretical MW (7,900) of discrete nanospheres with 86% vinyl groups of **V** cross-linked.

Fig. S11 Left: A toluene solution containing ~0.7 mM of **VI** with hydrolyzed silyl ester bonds in the presence of $PdCl_2$ solid. The yellow color indicated incorporation of Pd ion into **VI**. Right: Control, a toluene solution containing $PdCl_2$ solid.