

Supporting information

for

Multi POSS Cluster-Wrapped Polymers and Their Block Copolymers with A PEO Bottlebrush Polymer: Synthesis and Aggregation

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I. Experimental section

Materials

1-Aminopropyl-3,5,7,9,11,13,15-heptaisobutyl-POSS (POSS) was purchased from Hybrid Plastics Company and used without purification. *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride and 6-aminohexanoic acid are purchased from J&K and used directly. Triethylamine (Et₃N, Alfa-Aesar) is distilled over calcium hydride prior to use. Polyethylene oxide (PEO, $M_n=1000$ Da), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), 1-hydroxybenzotriazole (HOBT), 4-dimethylaminopyridine (DMAP), formic acid (HCOOH), methanol (MeOH), dichloromethane (CH₂Cl₂), chloroform (CHCl₃) and tetrahydrofuran (THF) are purchased from Alfa-Aesar. The Grubbs third generation catalyst is synthesized from Grubbs second generation catalyst (Sigma-Aldrich) following a procedure reported in literature.¹

Instrumentation and characterization

¹H and ¹³C Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400 MHz spectrometer in CDCl₃, and chemical shifts are given in ppm, referenced to the residual resonances of the solvents ($\delta = 7.26$ ppm for CHCl₃).

Fourier transform infrared (FT-IR) spectra were taken on a FT-IR spectrometer (Bio-Rad FTS-135) sampled with KBr pellet samples.

Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were acquired on a Bruker Autoflex III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All of the spectra were measured in positive reflection or linear mode.

The relative molecular weights was obtained using size exclusion chromatography (SEC), which was performed in THF at a flow rate of 0.2 mL/min at 30 °C on a Waters 1525 system equipped with three Waters Styragel columns, a Waters 2414 refractive index detector, in which narrow dispersed polystyrene (PS) as standards. The absolute molecular weights was obtained using size exclusion chromatography (SEC), which was performed in THF at a flow rate of 0.2 mL/min at 30 °C on a Viscotek 270max system equipped with a GPCmax isolated pump, an autosampler, three A6000M column, a 270max light scattering detector and a viscometer, with narrow dispersed polystyrene (PS) as standards.

Transmission electron microscopy (TEM) was performed using a field emission transmission electron microscopy FEI Tecnai G2F20 operating at an acceleration voltage of 200 kV. The samples were prepared by casting solutions on carbon film-coated copper grids. The mixed solvent was rapidly removed by using a piece of filter paper and then dried under vacuum at 25.0 °C for 24 h.

II. General Procedure for Synthesis of the Monomers

6-((3a*R*,4*R*,7*S*,7a*S*)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisindol-2-yl)hexanoic acid (5). A round-bottom flask is charged with *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (**1**) (4.00 g, 24.30 mmol) and 6-aminohexanoic acid (**2**) (3.3 g, 25.30 mmol). To the solid mixture is added toluene (50 mL) and Et₃N (410 μL, 2.92 mmol). The flask is fitted with a Dean-Stark trap and heated to reflux for 4 h. The mixture is then allowed to cool to room temperature and concentrated. The reaction mixture is diluted with CH₂Cl₂ (50 mL) and washed with 1 M aqueous HCl (2 × 20 mL). The organic layer is washed with saturated aqueous NaCl (20 mL), dried (Na₂SO₄), filtered, and concentrated under reduced pressure to provide **5** (6.35 g, 94%) as a white solid that is used without further purification: ¹H NMR (400 MHz,

CDCl₃): δ 6.25 (s, 2H), 3.43 (m, 2H), 3.23 (m, 2H), 2.64 (d, 2H, $J = 1.0$ Hz), 2.31 (t, 2H, $J = 7.2$ Hz), 1.65-1.46 (m, 5H), 1.32 (m, 2H), 1.18 (d, 1H, $J = 10.0$ Hz) (Fig. S1); ¹³C NMR (100 MHz, CDCl₃): δ 179.4, 178.2, 137.9, 47.8, 45.2, 42.8, 38.4, 33.8, 27.4, 26.4, 24.1 (Fig. S2).

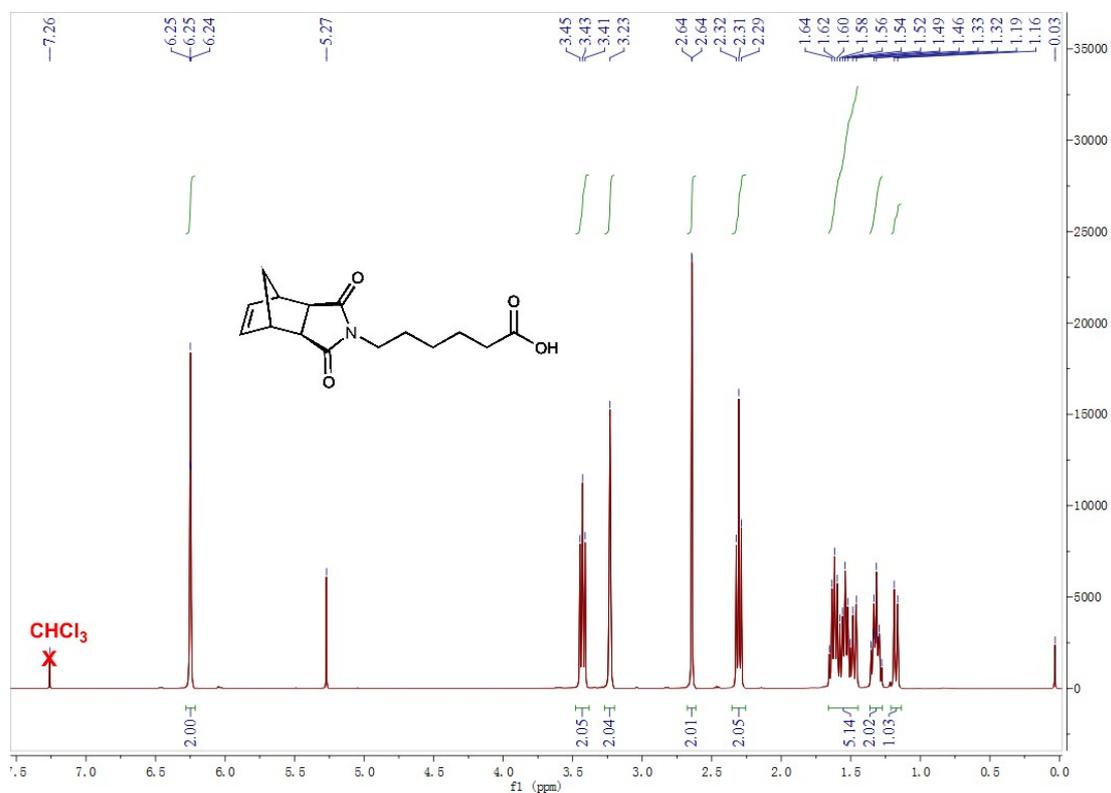


Fig. S1 ¹H NMR spectrum of compound 5.

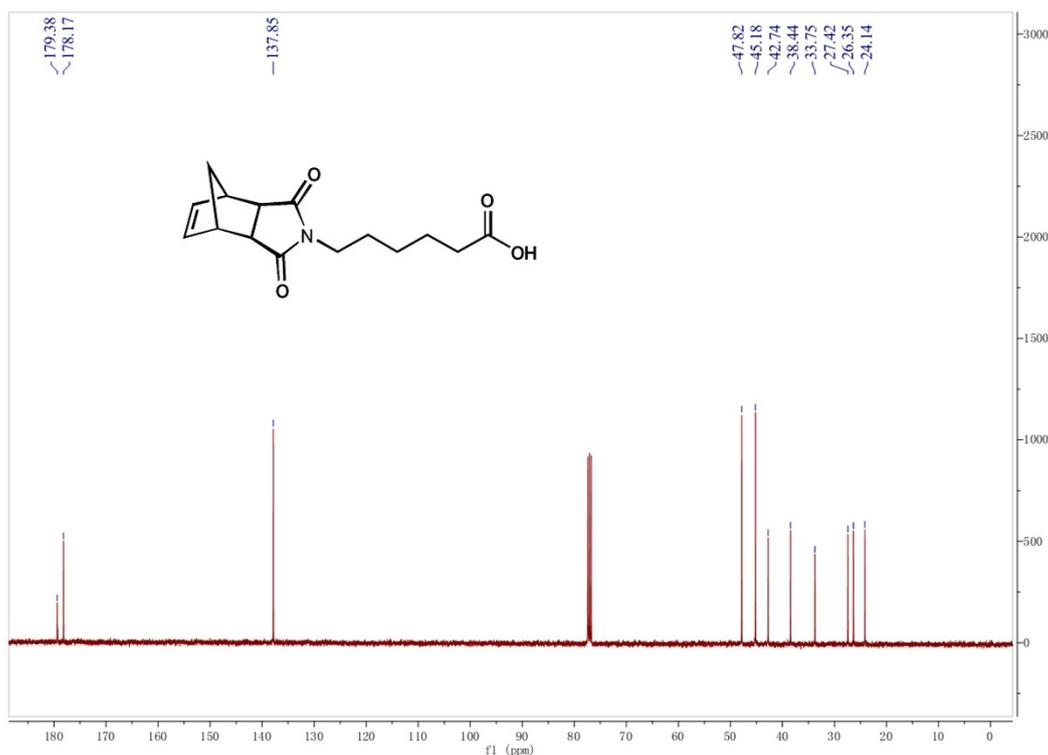


Fig. S2 ^{13}C NMR spectrum of compound **5**.

Norb-1POSS (6). A round-bottom flask is charged with **5** (1.39 g, 5.00 mmol), EDCI (1.15 g, 6.00 mmol) and HOBt (0.81 g, 5.98 mmol). To the solid mixture is added CH_2Cl_2 (25 mL). The flask is placed in an ice bath at $0\text{ }^\circ\text{C}$ under a nitrogen atmosphere and then a solution of POSS (5.25 g, 6.00 mmol) in CHCl_3 (25 mL) is added in 20 min. The reaction mixture is then stirred overnight at room temperature. The reaction mixture is washed orderly with H_2O (2×50 mL) and saturated aqueous NaCl (50 mL), dried (Na_2SO_4), filtered, concentrated to dryness and purified by flash chromatography (10% EtOAc in CH_2Cl_2) to give **6** as a white powder, 5.78g (85%). ^1H NMR (400 MHz, CDCl_3): δ 6.25 (s, 2H), 5.45 (s, 1H), 3.45 (t, 2H, $J = 8.0$ Hz), 3.26 (s, 2H), 3.22 (t, 2H, $J = 8.0$ Hz), 2.66 (s, 2H), 2.14 (t, 2H, $J = 8.0$ Hz), 1.65 (t, 2H, $J = 8.0$ Hz), 1.58 (m, 4H), 1.50 (d, 1H, $J = 12.0$ Hz), 1.32 (m, 2H), 1.20 (d, 1H, $J = 12.0$ Hz), 0.95 (d, 42H, $J = 8.0$ Hz), 0.59 (d, 16H, $J = 8.0$ Hz) (Fig. S3); ^{13}C NMR (100 MHz, CDCl_3): δ 178.1, 172.5, 137.9, 47.8, 45.2, 42.8, 41.8, 38.4, 36.5, 27.5, 26.6, 25.7, 25.2, 23.9, 23.8, 23.1, 22.5, 22.4 (Fig. S4); MALDI-TOF-MS: calcd. for $\text{C}_{46}\text{H}_{88}\text{N}_2\text{O}_{15}\text{Si}_8$ $[\text{M}+\text{H}]^+$ 1133.44, found 1133.46; $[\text{M}+\text{Na}]^+$ 1155.42, found 1155.43, $[\text{M}+\text{k}]^+$ 1171.39, found 1171.40 (Fig. S5).

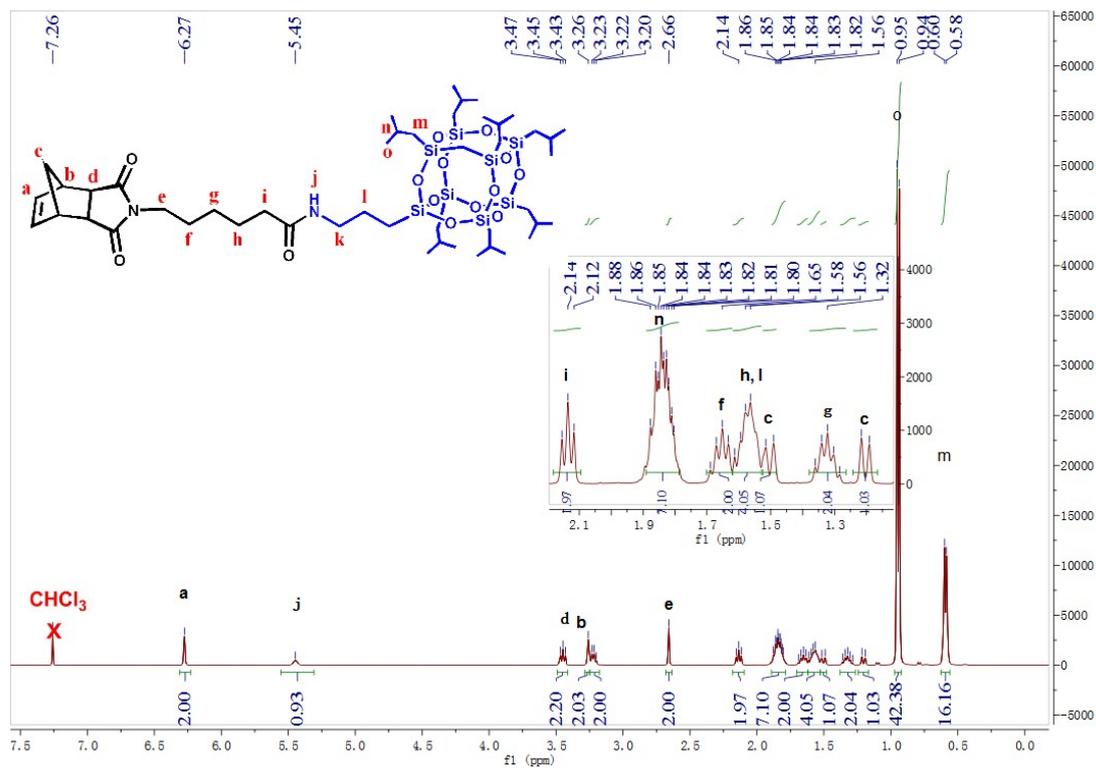


Fig. S3 ^1H NMR spectrum of compound 6.

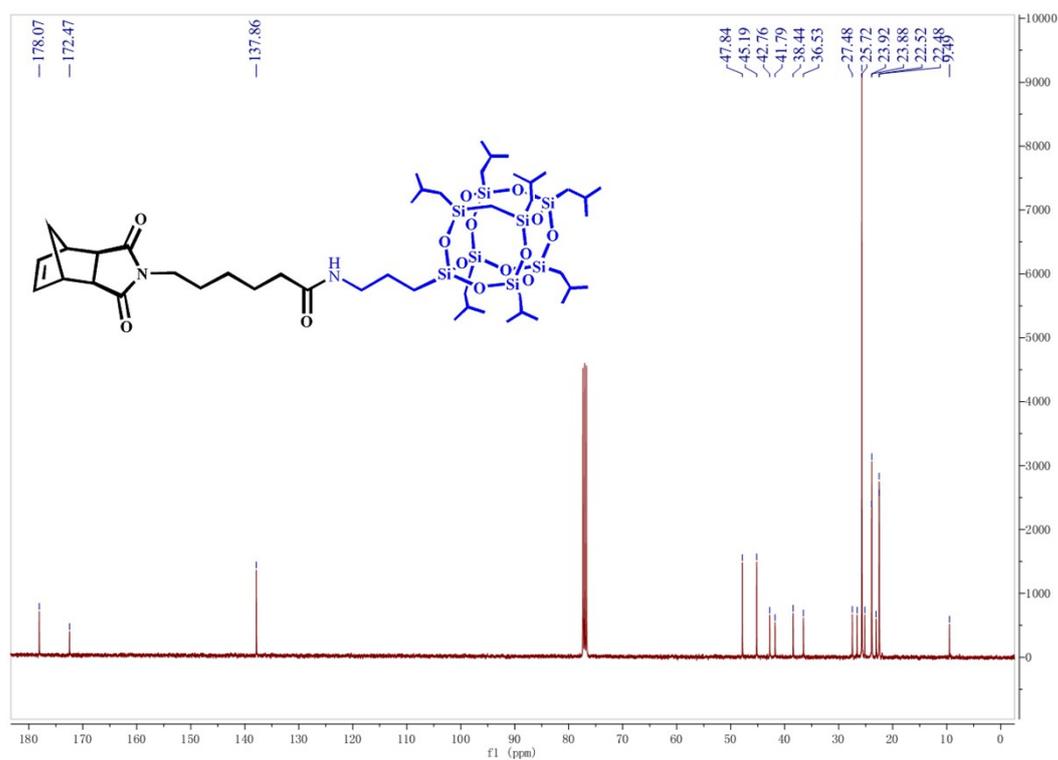


Fig. S4 ^{13}C NMR spectrum of compound 6.

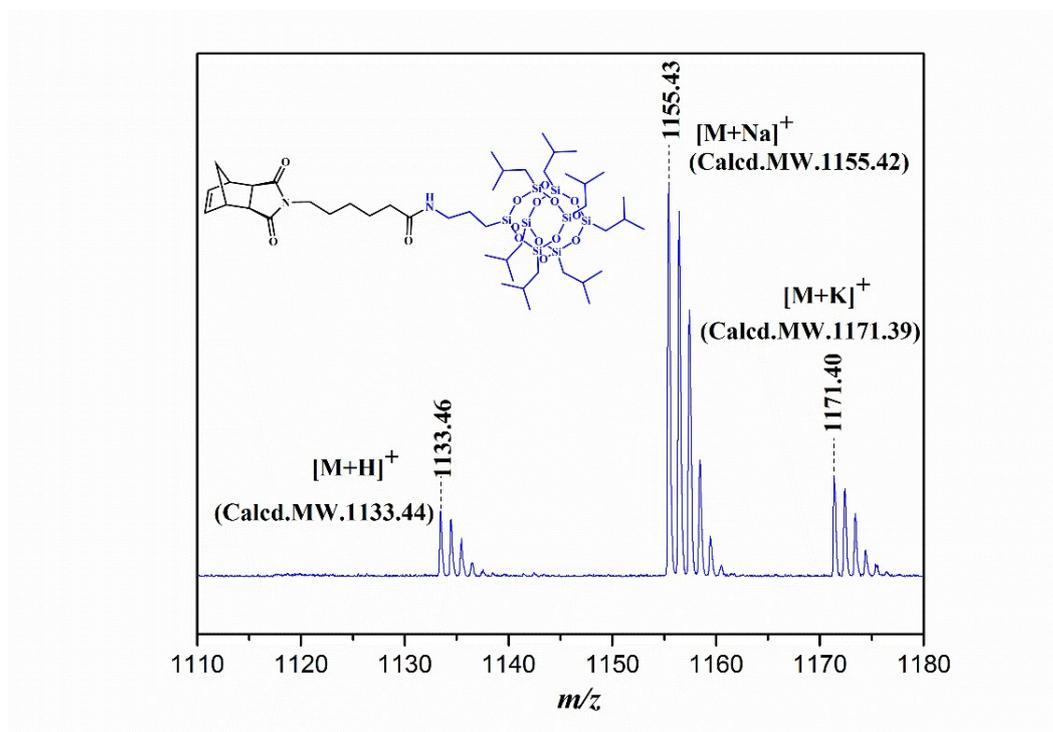


Fig. S5 MALDI-TOF mass spectrum of compound 6.

Di-*tert*-butyl-5-(6-((3*aR*,4*R*,7*S*,7*aS*)-1,3-dioxo-1,3,3*a*,4,7,7*a*-hexahydro-2*H*-4,7-methanoisindol-2-yl)hexanamido)-5-methylnonanedioate (7). **5** (1.50 g, 5.41 mmol), CH₂Cl₂ (30 mL), di-*tert*-butyl-4-Amino-4-methylheptanedioate (**3**) (1.95 g, 6.49 mmol), EDCI (1.04 g, 5.41 mmol) and DMAP (0.07 g, 0.54 mmol) are added to a 100 mL round-bottom flask. The reaction mixture is then stirred overnight at room temperature. The reaction mixture is washed orderly with H₂O (2 × 50 mL) and saturated aqueous NaCl (50 mL), dried (Na₂SO₄), filtered, concentrated to dryness and purified by flash chromatography (25% EtOAc in PE) to give **7** as a white powder, 2.79g (92%). ¹H NMR (400 MHz, CDCl₃): δ 6.29 (s, 2H), 5.90 (s, 1H), 3.45 (t, 2H, *J* = 8.0 Hz), 3.26 (s, 2H), 2.68 (s, 2H), 2.24 (t, 2H, *J* = 8.0 Hz), 2.07 (m, 4H), 1.89 (m, 2H), 1.58 (m, 4H), 1.50 (d, 1H, *J* = 12.0 Hz), 1.32 (t, 2H, *J* = 8.0 Hz), 1.27 (s, 3H), 1.22 (d, 1H, *J* = 12.0 Hz) (Fig. S6); ¹³C NMR (100 MHz, CDCl₃): δ 177.9, 173.1, 172.2, 137.7, 80.4, 55.1, 47.7, 45.1, 42.7, 38.4, 37.0, 33.3, 30.2, 28.0, 27.7, 26.5, 25.1, 23.7 (Fig. S7); MALDI-TOF-MS: calcd. for C₃₁H₄₈N₂O₇ [M+Na]⁺ 583.33, found 583.37; [M+K]⁺ 599.31, found 599.34 (Fig. S8).

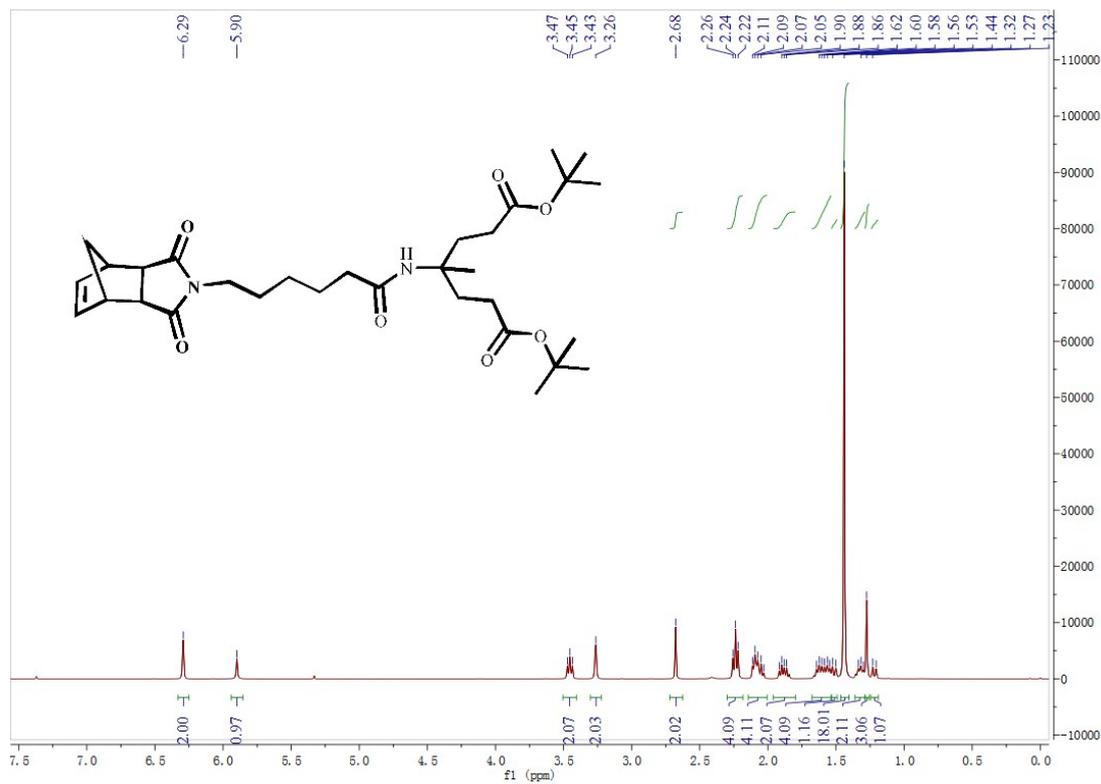


Fig. S6 ¹H NMR spectrum of compound 7.

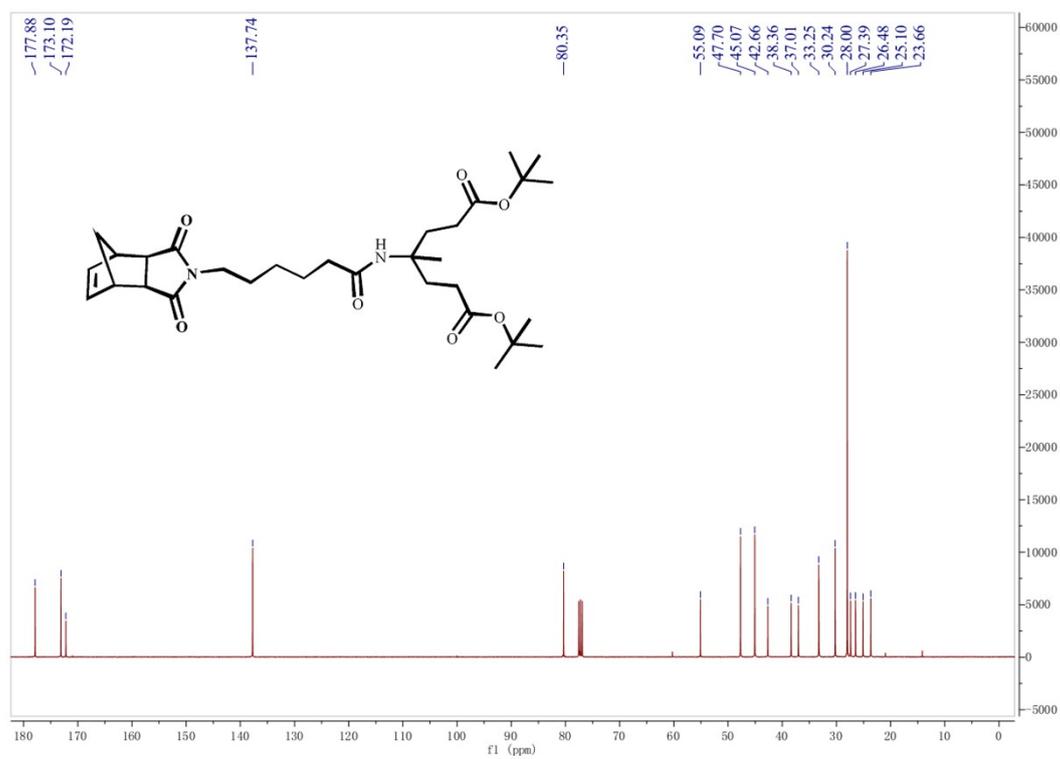


Fig. S7 ¹³C NMR spectrum of compound 7.

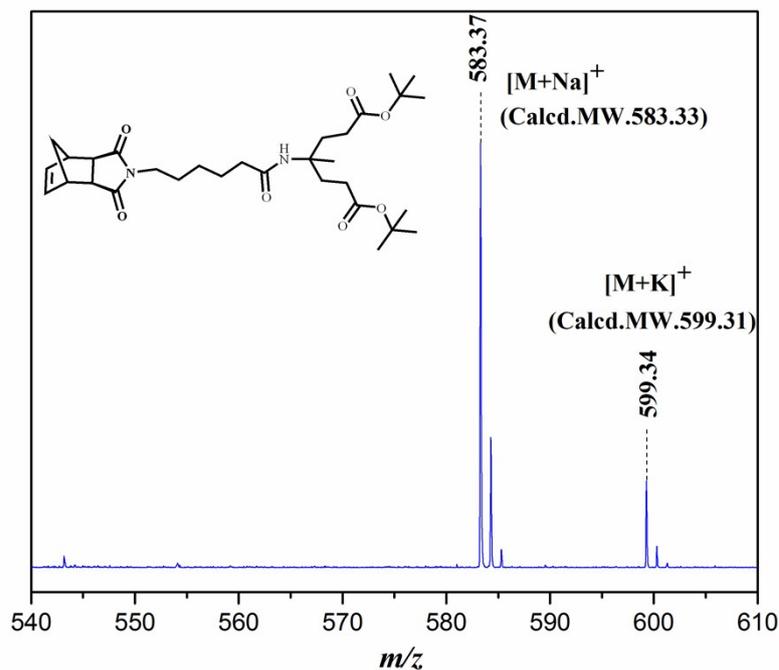


Fig. S8 MALDI-TOF mass spectrum of compound 7.

Norb-2POSS (8). A round-bottom flask is charged with **7** (1.90 g, 3.39 mmol) and HCOOH (20 mL). The reaction mixture is then stirred overnight at room temperature, then concentrated under reduced pressure. To the flask is added $CHCl_3$ (25 mL), EDCI (1.43 g, 7.46 mmol) and DMAP (0.09 g, 0.75 mmol). The flask is placed in an ice bath at 0 °C under a nitrogen atmosphere and then a solution of POSS (6.52 g, 7.46 mmol) in $CHCl_3$ (25 mL) is added in 15 min. The reaction mixture is then stirred overnight at room temperature. The reaction mixture is washed orderly with H_2O (2×50 mL) and saturated aqueous NaCl (50 mL), dried (Na_2SO_4), filtered, concentrated to dryness and purified by flash chromatography (10% EtOAc in CH_2Cl_2) to give **8** as a white powder, 6.30g (86%). 1H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 1H), 6.28 (s, 2H), 5.88 (s, 2H), 3.45 (t, 2H, $J = 8.0$ Hz), 3.25-3.14 (s, 6H), 2.66 (s, 2H), 2.22 (m, 4H), 2.10 (t, 2H, $J = 8.0$ Hz), 2.06-1.93 (m, 4H), 1.85 (m, 14H), 1.57 (m, 9H), 1.32 (m, 5H), 1.21 (d, 1H, $J = 12.0$ Hz), 0.95 (d, 84H, $J = 8.0$ Hz), 0.59 (d, 32H, $J = 8.0$ Hz) (Fig. S9); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 173.2, 172.8, 137.8, 55.32, 47.8, 45.2, 42.8, 42.1, 38.6, 37.1, 34.5, 31.3, 27.6, 26.6, 25.7, 25.1, 23.9, 23.8, 23.0, 22.5, 22.4, 22.0 (Fig. S10); MALDI-TOF-MS: calcd. for $C_{85}H_{170}N_4O_{29}Si_{16}$ $[M+Na]^+$ 2184.64, found 2184.75; $[M+K]^+$ 2200.75, found 2200.72 (Fig. S11).

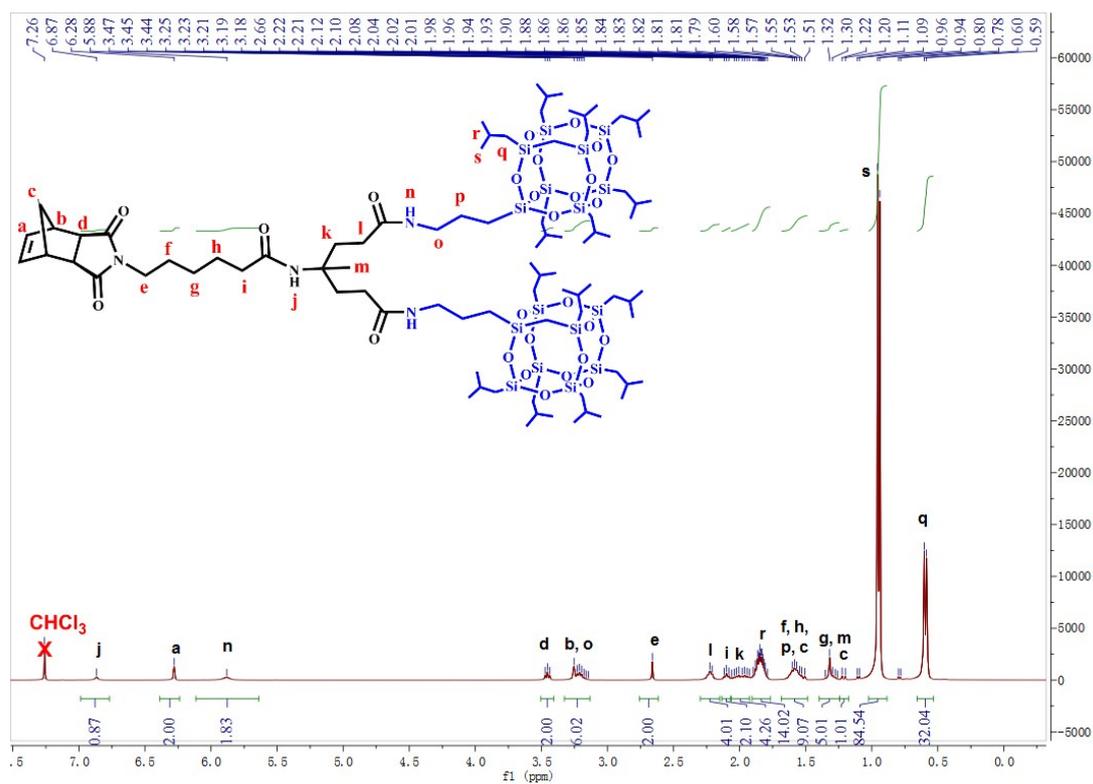


Fig. S9 ^1H NMR spectrum of compound **8**.

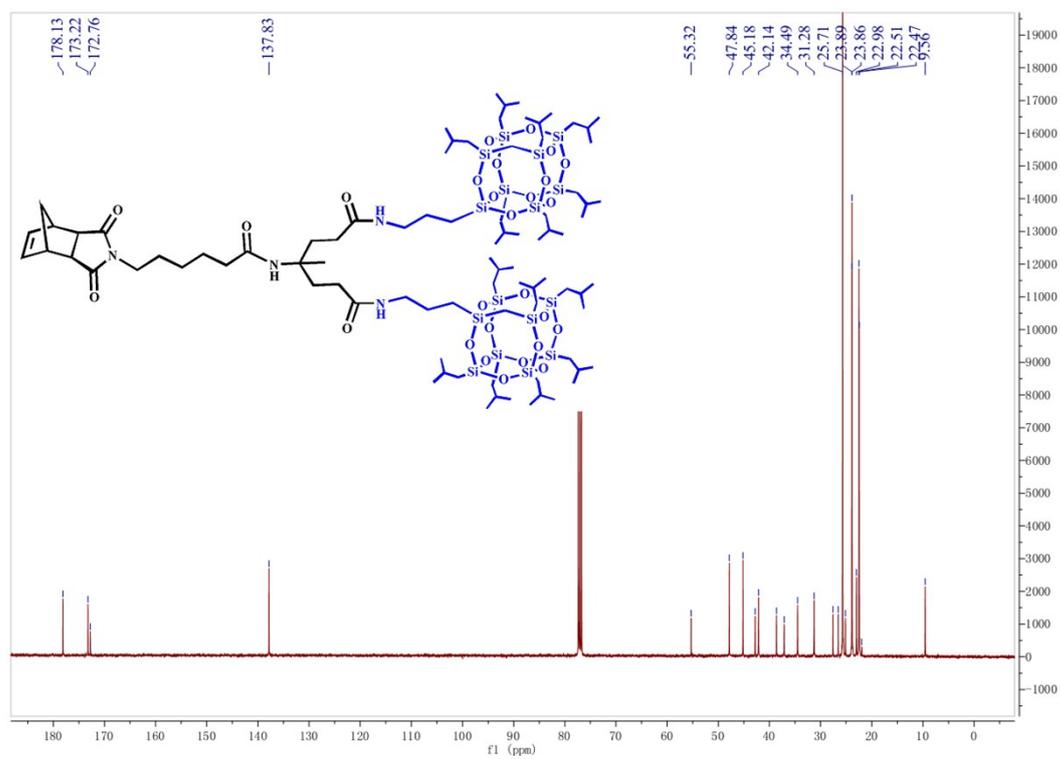


Fig. S10 ^{13}C NMR spectrum of compound **8**.

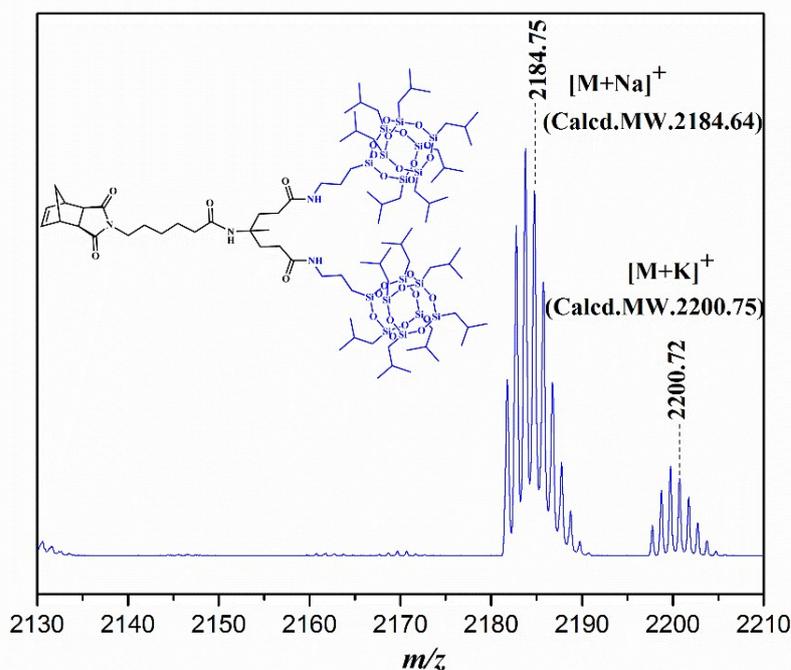


Fig. S11 MALDI-TOF mass spectrum of compound **8**.

Di-*tert*-butyl-4-(3-(*tert*-butoxy)-3-oxopropyl)-4-(6-((3*aR*,4*R*,7*S*,7*aS*)-1,3-dioxo-1,3,3*a*,4,7,7*a*-hexahydro-2*H*-4,7-methanoisindol-2-yl)hexanamido)heptanedioate (9**).** **5** (2.77 g, 10.00 mmol), CHCl₃ (50 mL), tri-*tert*-butyl-4-Amino-4-methylheptanedioate (**4**) (4.56 g, 11.00 mmol), EDCI (2.11 g, 11.00 mmol) and DMAP (0.13 g, 1.10 mmol) are added to a 100 mL round-bottom flask. The reaction mixture is then stirred overnight at room temperature. The reaction mixture is washed orderly with H₂O (2 × 100 mL) and saturated aqueous NaCl (100 mL), dried (Na₂SO₄), filtered, concentrated to dryness and purified by flash chromatography (25% EtOAc in PE) to give **9** as a white powder, 6.40g (95%). ¹H NMR (400 MHz, CDCl₃): δ 6.28 (s, 2H), 5.86 (s, 1H), 3.46 (t, 2H, *J* = 8.0 Hz), 3.27 (s, 2H), 2.67 (s, 2H), 2.21 (t, 6H, *J* = 8.0 Hz), 2.10 (t, 2H, *J* = 8.0 Hz), 1.96 (t, 6H, *J* = 8.0 Hz), 1.64-1.55 (m, 5H), 1.52 (d, 1H, *J* = 12.0 Hz), 1.44 (s, 27H), 1.36-1.28 (m, 2H), 1.22 (d, 1H, *J* = 12.0 Hz) (Fig. S12); ¹³C NMR (100 MHz, CDCl₃): δ 178.0, 172.9, 172.2, 137.8, 80.6, 57.3, 47.8, 45.2, 42.7, 38.4, 37.2, 30.4, 29.9, 28.1, 27.4, 26.6, 25.2 (Fig. S13); MALDI-TOF-MS: calcd. for C₃₇H₅₇N₂O₉ [M+Na]⁺ 697.40, found 697.44 (Fig. S14).

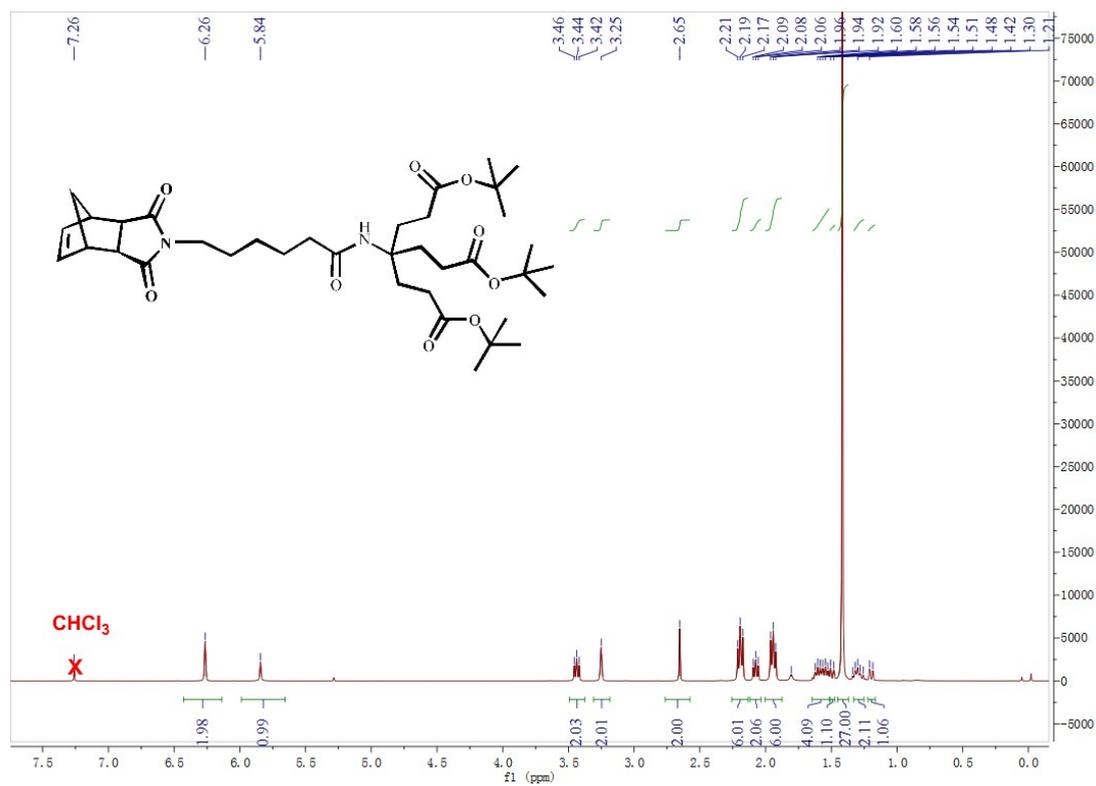


Fig. S12 ¹H NMR spectrum of compound 9.

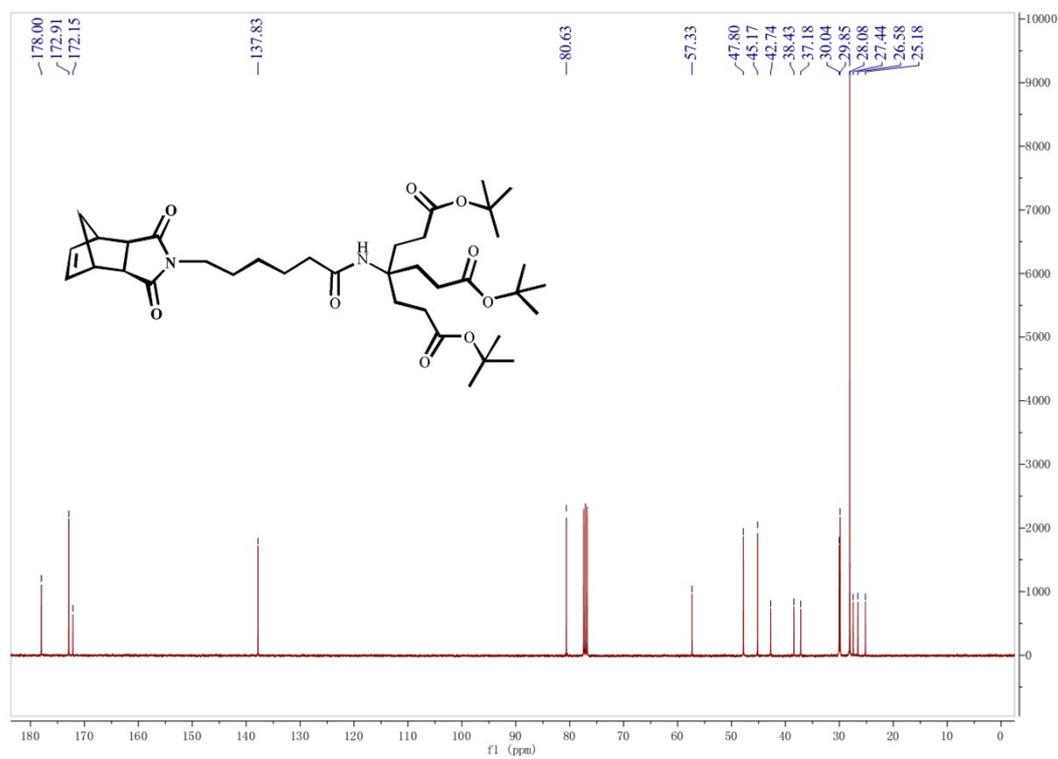


Fig. S13 ¹³C NMR spectrum of compound 9.

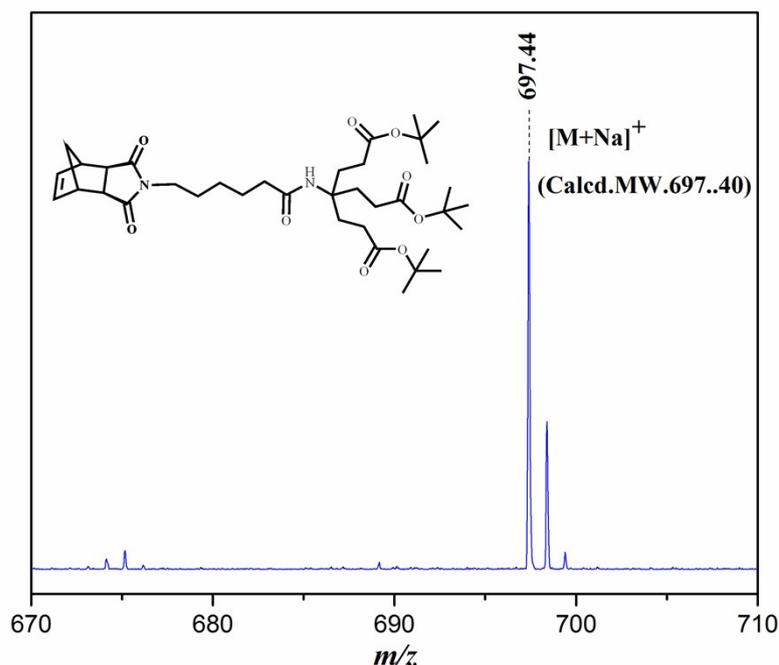


Fig. S14 MALDI-TOF mass spectrum of compound **9**.

Norb-3POSS (10). A round-bottom flask is charged with **9** (1.44 g, 2.13 mmol) and HCOOH (20 mL). The reaction mixture is then stirred overnight at room temperature, then concentrated under reduced pressure. To the flask is added CHCl₃ (25 mL), EDCI (1.35 g, 7.04 mmol) and DMAP (0.09 g, 0.70 mmol). The flask is placed in an ice bath at 0 °C under a nitrogen atmosphere and then a solution of POSS (6.16 g, 7.04 mmol) in CHCl₃ (25 mL) is added in 15 min. The reaction mixture is then stirred overnight at room temperature. The reaction mixture is washed orderly with H₂O (2 × 50 mL) and saturated aqueous NaCl (50 mL), dried (Na₂SO₄), filtered, concentrated to dryness and purified by flash chromatography (10% EtOAc in CH₂Cl₂) to give **10** as a white powder, 5.43g (83%). ¹H NMR (400 MHz, CDCl₃): δ 7.08 (s, 1H), 6.28 (s, 2H), 5.90 (t, 2H, *J* = 4.0 Hz), 3.46 (t, 2H, *J* = 8.0 Hz), 3.25 (s, 2H), 3.19 (q, 6H, *J* = 8.0 Hz), 2.66 (s, 2H), 2.20 (t, 6H, *J* = 8.0 Hz), 2.10 (t, 2H, *J* = 8.0 Hz), 2.04-2.00 (m, 6H), 1.88-1.80 (m, 21H), 1.61-1.51 (m, 11H), 1.33-1.25 (m, 3H), 1.21 (d, 1H, *J* = 8.0 Hz), 0.94 (d, 126H, *J* = 4.0 Hz), 0.59 (d, 32H, *J* = 8.0 Hz) (Fig. S15); ¹³C NMR (100 MHz, CDCl₃): δ 178.2, 173.1, 172.7, 137.8, 57.7, 47.8, 45.2, 42.8, 42.2, 38.6, 37.0, 31.4, 31.0, 27.6, 26.5, 25.7, 25.5, 25.1, 23.9, 23.8, 23.0, 22.5, 22.4, 22.0, 21.9 (Fig. S16); MALDI-TOF-MS: calcd. for C₁₁₇H₂₃₉N₅O₄₂Si₂₄ [M+Na]⁺ 3099.24, found 3098.86

(Fig. S17).

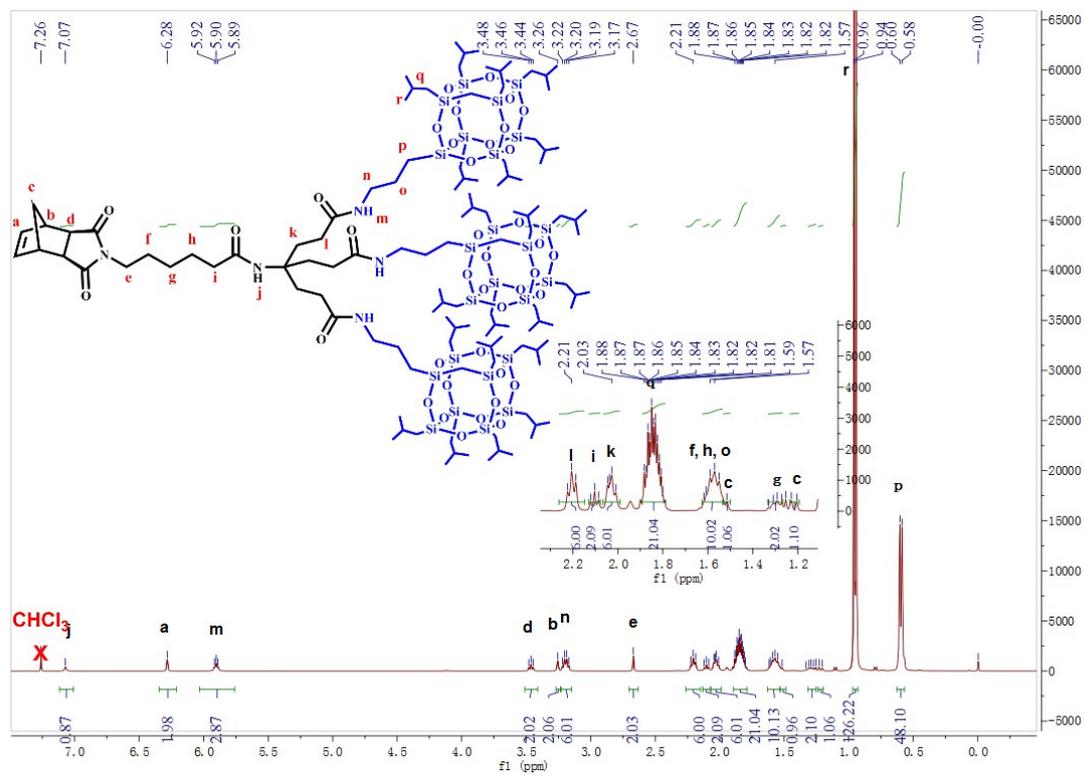


Fig. S15 ¹H NMR spectrum of compound 10.

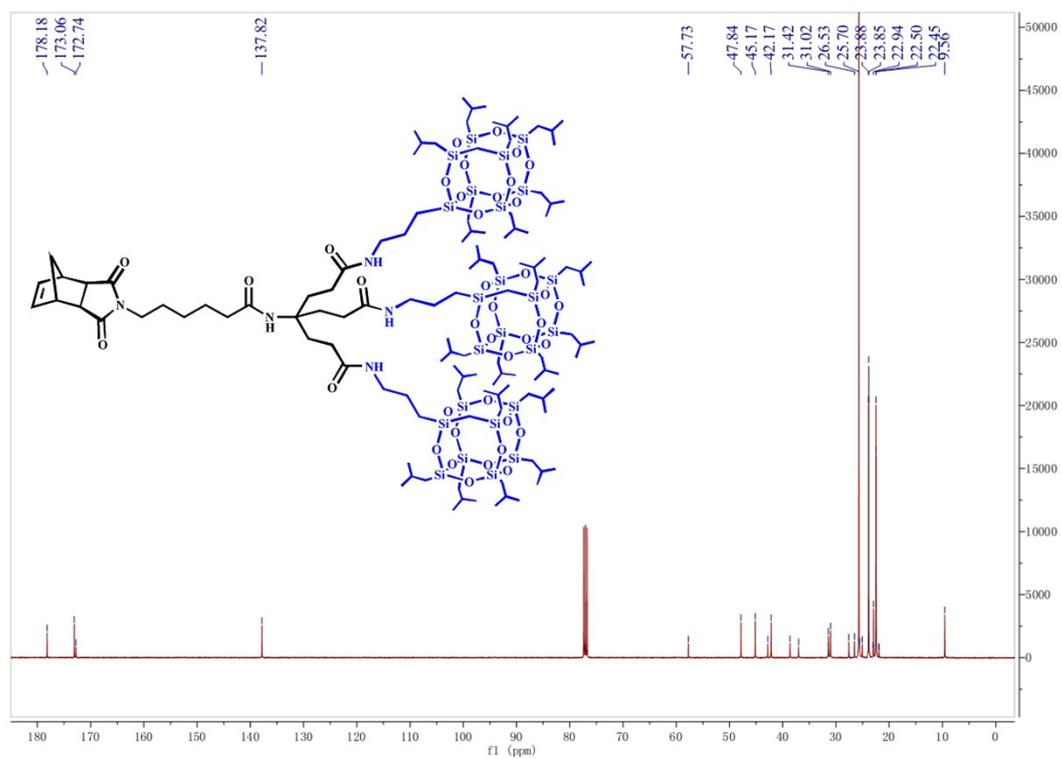


Fig. S16 ¹³C NMR spectrum of compound 10.

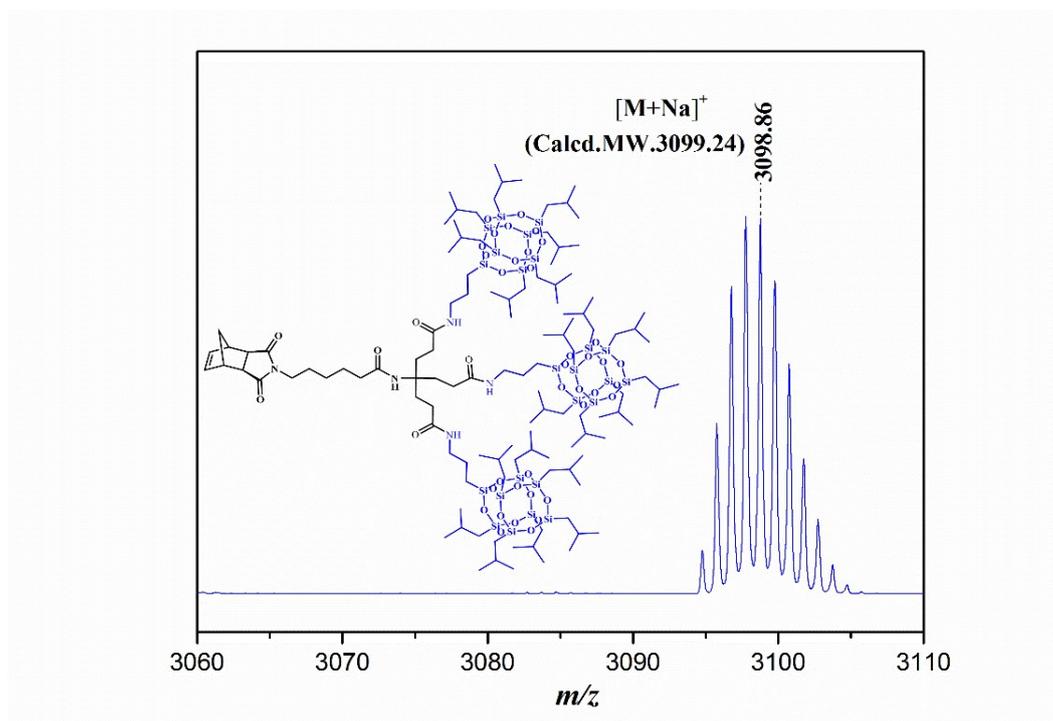


Fig. S17 MALDI-TOF mass spectrum of compound **10**.

Tetra-*tert*-butyl-4,4'-((4-(6-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisindol-2-yl)hexanamido)-4-methylheptanedioyl)bis(azanediyl))bis(4-methylheptanedioate) (11). A round-bottom flask is charged with **7** (3.49 g, 6.22 mmol) and HCOOH (50 mL). The reaction mixture is then stirred overnight at room temperature, then concentrated under reduced pressure. Then di-*tert*-butyl-4-Amino-4-methylheptanedioate (**3**) (4.12 g, 13.70 mmol), CHCl₃ (60 mL), EDCI (2.62 g, 13.70 mmol) and DMAP (0.17 g, 1.37 mmol) are added and stirred overnight at room temperature. The reaction mixture is washed orderly with H₂O (2 × 100 mL) and saturated aqueous NaCl (100 mL), dried (Na₂SO₄), filtered, concentrated to dryness and purified by flash chromatography (25% EtOAc in PE) to give **11** as a white powder, 5.74g (91%). ¹H NMR (400 MHz, CDCl₃): δ 6.78 (s, 1H), 6.26 (s, 2H), 6.22 (s, 2H), 3.39 (t, 2H, *J* = 8.0 Hz), 3.19 (s, 2H), 2.61 (s, 2H), 2.15 (t, 8H, *J* = 8.0 Hz), 2.10 (t, 4H, *J* = 8.0 Hz), 2.05-1.97 (m, 6H), 1.93-1.76 (m, 8H), 1.56-1.44 (m, 6H), 1.37 (s, 36H), 1.22 (m, 5H), 1.18 (m, 7H) (Fig. S18); ¹³C NMR (100 MHz, CDCl₃): δ 178.0, 172.9, 172.2, 137.8, 80.6, 57.3, 47.8, 45.2, 42.7, 38.4, 37.2, 30.0, 29.9, 28.1, 27.4, 26.6, 25.2 (Fig. S19), MALDI-TOF-MS: calcd. for C₅₅H₉₀N₄O₁₃ [M+Na]⁺ 1037.64, found 1037.72;

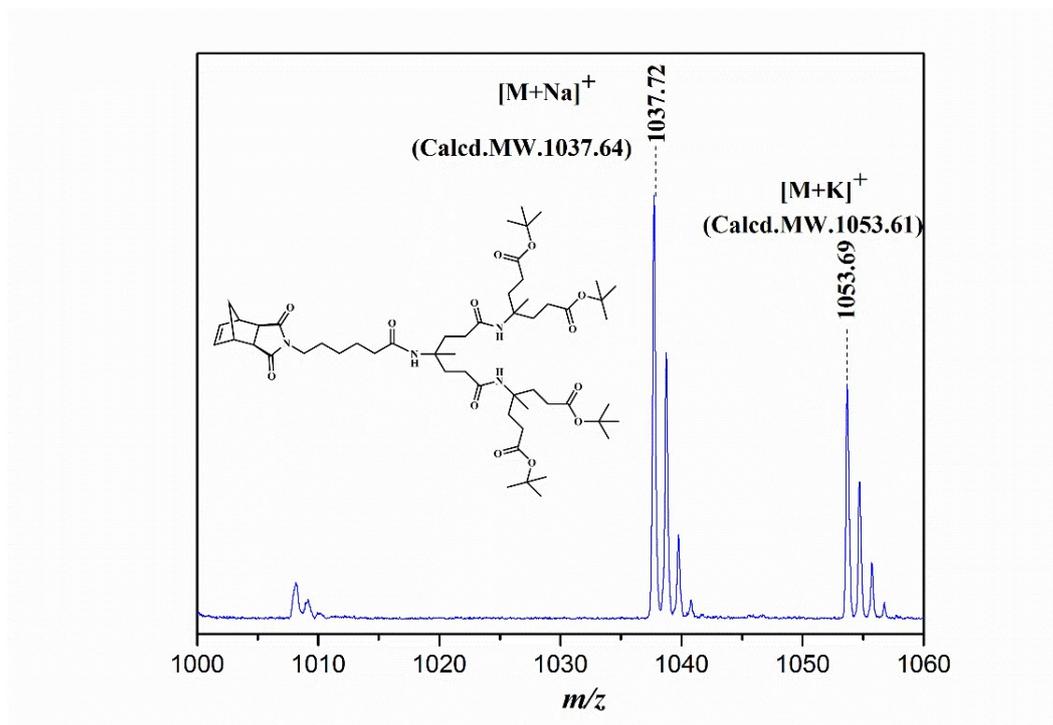


Fig. S20 MALDI-TOF mass spectrum of compound **11**.

Norb-4POSS (12). A round-bottom flask is charged with **11** and HCOOH (30 mL). The reaction mixture is then stirred overnight at room temperature, then concentrated under reduced pressure. To the flask is added CHCl₃ (30 mL), EDCI (0.86 g, 4.51 mmol) and DMAP (0.06 g, 0.45 mmol). The flask is placed in an ice bath at 0 °C under a nitrogen atmosphere and then a solution of POSS (3.94 g, 4.51 mmol) in CHCl₃ (30 mL) is added in 25 min. The reaction mixture is then stirred overnight at room temperature. The reaction mixture is washed orderly with H₂O (2 × 100 mL) and saturated aqueous NaCl (100 mL), dried (Na₂SO₄), filtered, concentrated to dryness and purified by flash chromatography (10% EtOAc in CH₂Cl₂) to give **12** as a white powder, 3.54g (82%). ¹H NMR (400 MHz, CDCl₃): δ 7.13 (s, 1H), 7.06 (s, 2H), 6.25 (s, 2H), 6.06 (s, 4H), 3.42 (t, 4H, *J* = 8.0 Hz), 3.21 (s, 3H), 3.17 (m, 7H), 2.81 (m, 1H), 2.64 (s, 2H), 2.17 (s, 12H), 2.09-2.00 (m, 7H), 1.89 (m, 7H), 1.82 (m, 28H), 1.55 (m, 12H), 1.27 (s, 10H), 1.17 (d, 1H, *J* = 12.0 Hz), 0.92 (d, 128H, *J* = 8.0 Hz), 0.56 (d, 64H, *J* = 8.0 Hz) (Fig. S21); ¹³C NMR (100 MHz, CDCl₃): δ 178.1, 173.5, 173.1, 173.0, 137.8, 55.5, 55.4, 50.33, 47.8, 45.1, 42.8, 42.1, 38.6, 37.2, 34.5, 34.3, 32.0, 31.3, 31.2, 28.1, 27.5, 26.5, 25.9, 25.7, 25.5, 25.2, 24.0, 23.9, 23.8, 23.7, 23.0, 22.5, 22.4, 22.0, 21.9 (Fig. S22); MALDI-TOF-MS: calcd. for C₈₅H₁₇₀N₄O₂₉Si₁₆ [M+Na]⁺

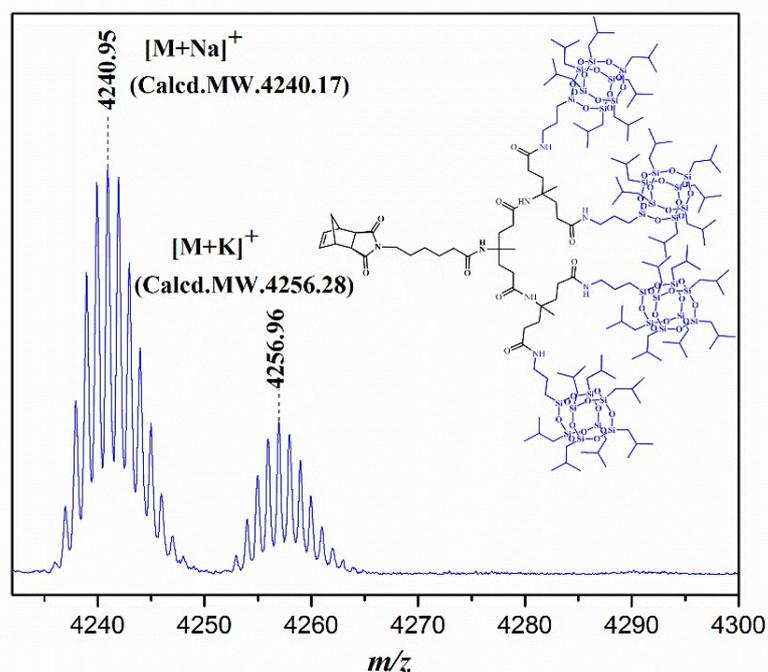


Fig. S23 MALDI-TOF mass spectrum of compound **12**.

Norb-PEO (13). A round-bottom flask is charged with **5** (2.80 g, 10.00 mmol) and CH_2Cl_2 (40 mL). To the flask is added EDCI (1.91 g, 11.00 mol), DMAP (0.12g, 1.10 mmol) and polyethylene oxide (PEO) (9.08 g, 9.08 mmol). The reaction mixture is then stirred overnight at room temperature. The reaction mixture is diluted with CH_2Cl_2 (50 mL) and washed with H_2O (3×40 mL). The organic layer is washed with saturated aqueous NaCl (20 mL), dried (Na_2SO_4), filtered, concentrated to dryness and purified by flash chromatography (10% MeOH in CH_2Cl_2) to provide **13** (10.63 g, 93%) as a white Semi-Solid. ^1H NMR (400 MHz, CDCl_3): δ 6.21 (s, 2H), 4.03 (dd, 4H, $J = 8.0$ Hz), 3.56 (m, 76H), 3.38 (t, 2H, $J = 8.0$ Hz), 3.29 (s, 3H), 3.19 (s, 2H), 2.59 (s, 2H), 2.20 (t, 2H, $J = 8.0$ Hz), 1.56 (t, 2H, $J = 8.0$ Hz), 1.49 (t, 2H, $J = 8.0$ Hz), 1.43 (d, 1H, $J = 8.0$ Hz), 1.25 (t, 2H, $J = 8.0$ Hz), 1.17 (t, 4H, $J = 8.0$ Hz), 1.13 (d, 1H, $J = 8.0$ Hz) (Fig. S24).

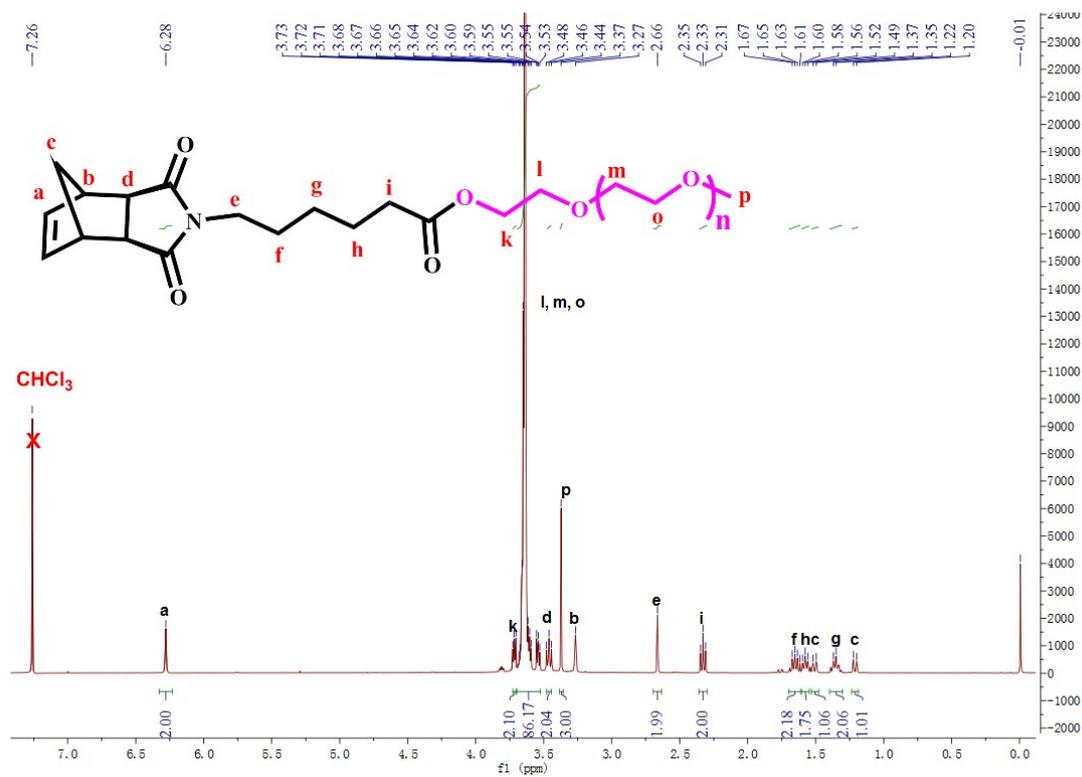


Fig. S24 ¹³C NMR spectrum of compound 13.

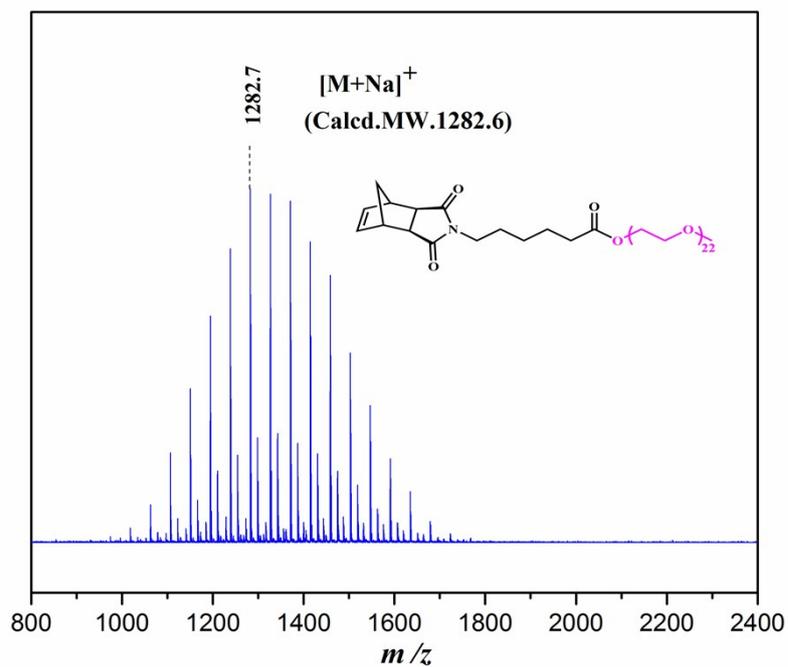


Fig. S25 MALDI-TOF mass spectrum of compound 13.

II. General Procedure for Synthesis of the polymers and block copolymers

General procedure for the synthesis of polymers.

A solution of Norb-*m*POSS (0.1 mmol/mL CH₂Cl₂) is placed in a flask with stir bar. The polymerization is initiated by quickly adding a solution of the appropriate amount of Grubbs third generation catalyst solution (0.01 mmol/mL CH₂Cl₂). The mixture is stirred until no residual monomer is left (determined via GPC). The polymerization is terminated with ethyl vinyl ether (0.2 mL) before the product is precipitated in ice-cold methanol. The polymer is dried in a vacuum oven yielding 70-90% of a grayish solid. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 5.77, 5.51 (polymer backbone and CH=CH), 0.96 [CH(CH₃)₂], 0.60 (SiCH₂) (Fig.s S26-S29). FT-IR (KBr, cm⁻¹): 1770 (asymmetric imide C=O stretching), 1701 (symmetric imide C=O stretching), 2958-2875 (isobutyl C-H stretch) and 1110 (Si-O-Si stretching of POSS core) (Fig. S30). Poly(Norb-PEO) polymer is synthesized as the poly(Norb-*m*POSS) polymer method.

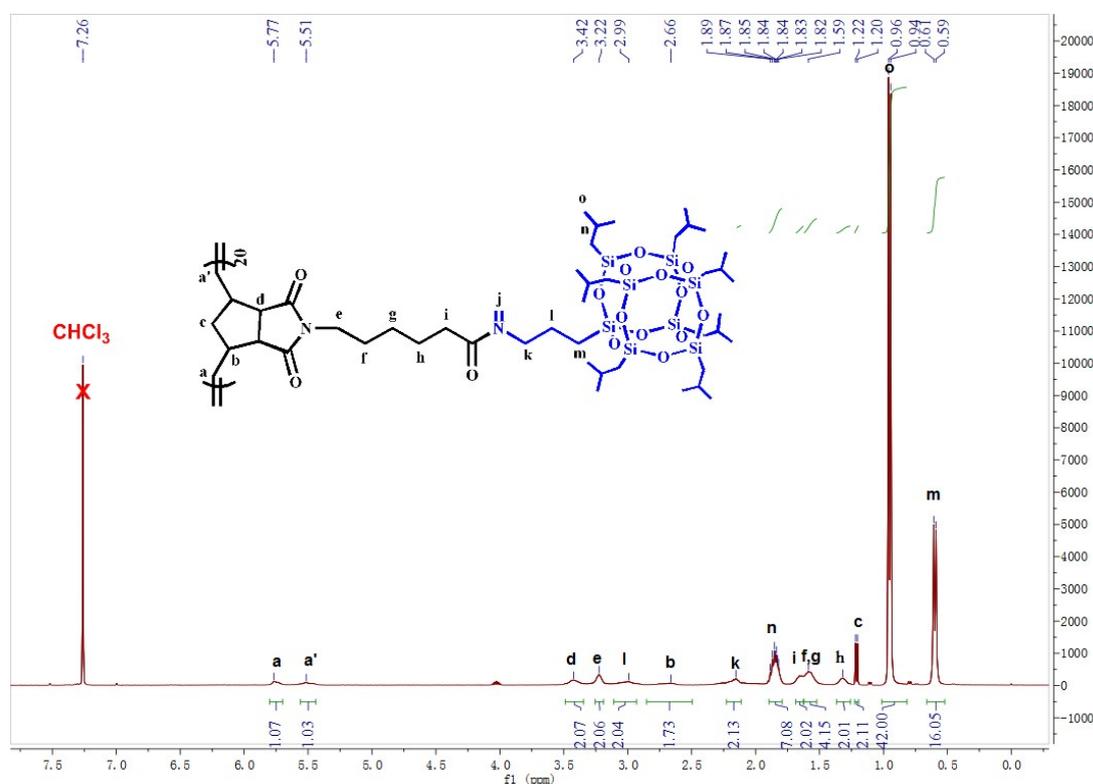


Fig. S26 ¹H NMR spectrum of poly(Norb-1POSS)₂₀.

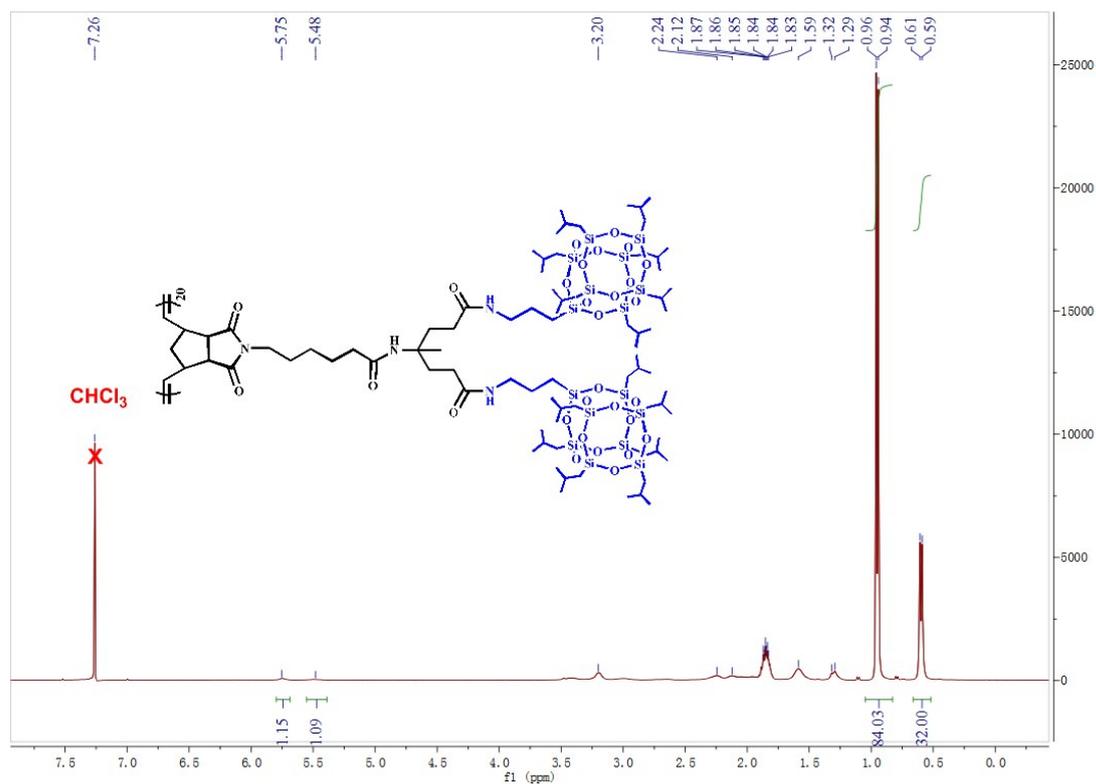


Fig. S27 ¹H NMR spectrum of poly(Norb-2POSS)₂₀.

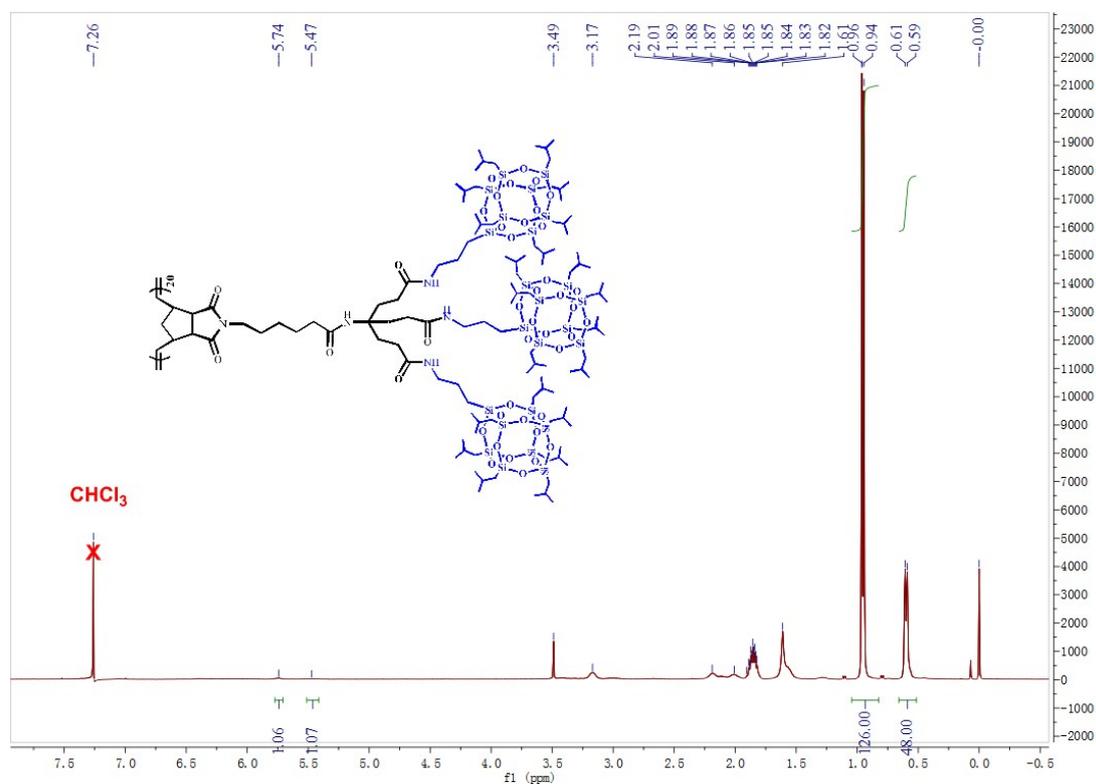


Fig. S28 ¹H NMR spectrum of poly(Norb-3POSS)₂₀.

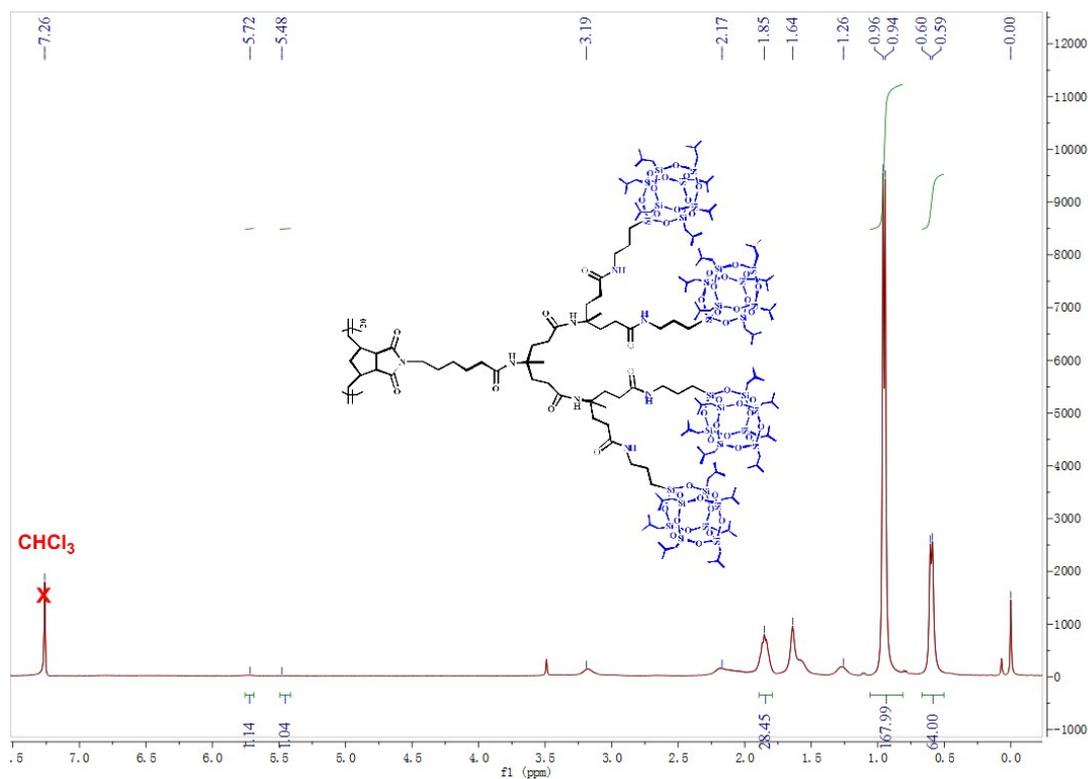


Fig. S29 ^1H NMR spectrum of poly(Norb-4POSS) $_{20}$.

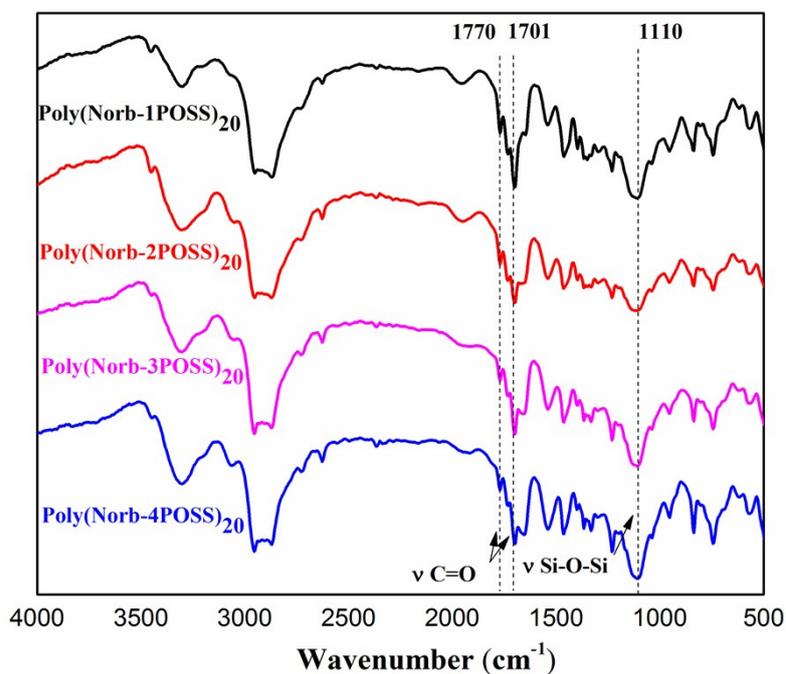


Fig. S30 FT-IR spectra of poly(Norb- m POSS) $_{20}$.

General procedure for the synthesis of block copolymers.

A solution of Norb- m POSS (0.1 mmol/mL CH_2Cl_2) is placed in a flask with stir bar. The

polymerization is initiated by quickly adding a solution of the appropriate amount of Grubbs third generation catalyst solution (0.01 mmol/mL CH_2Cl_2). The reaction is stirred vigorously under open air at room temperature for 2 hours. Upon complete monomer conversion a solution of compound Norb-PEO (0.1 mmol/mL CH_2Cl_2) is added via syringe, and the mixture is stirred until no residual monomer is left (determined via GPC). The polymerization is terminated with ethyl vinyl ether (0.2 mL) before the product is precipitated in ice-cold methanol. The block copolymer is dried in a vacuum oven yielding 70-90% of a brownish solid. ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 5.77, 5.51 (polymer backbone and $\text{CH}=\text{CH}$), 3.64 (OCH_2CH_2), 0.96 [$\text{CH}(\text{CH}_3)_2$], 0.60 (SiCH_2) (Fig.s S31-S34). FT-IR (KBr, cm^{-1}): 1770 (asymmetric imide $\text{C}=\text{O}$ stretching), 1701 (symmetric imide $\text{C}=\text{O}$ stretching), 2958-2875 (isobutyl $\text{C}-\text{H}$ stretching), and 1110 ($\text{Si}-\text{O}-\text{Si}$ stretching of POSS core) (Fig. S35).

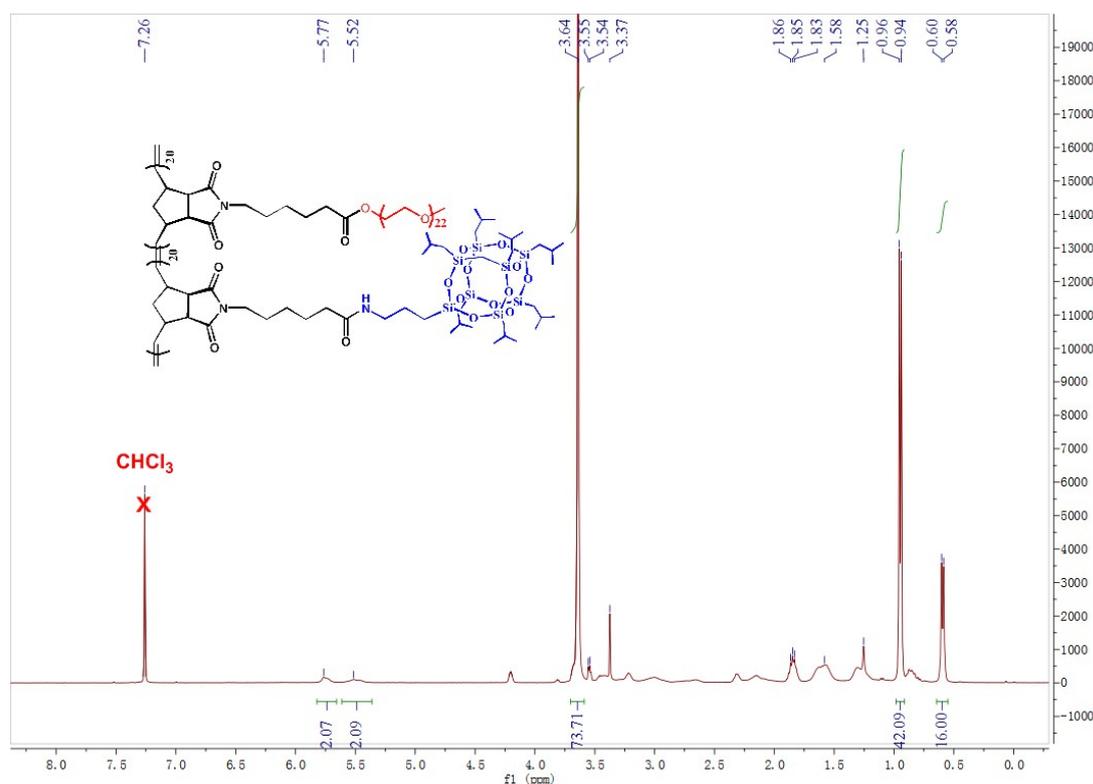


Fig. S31 ^1H NMR spectrum of poly(Norb-1POSS)₂₀-b-poly(Norb-PEO)₂₀.

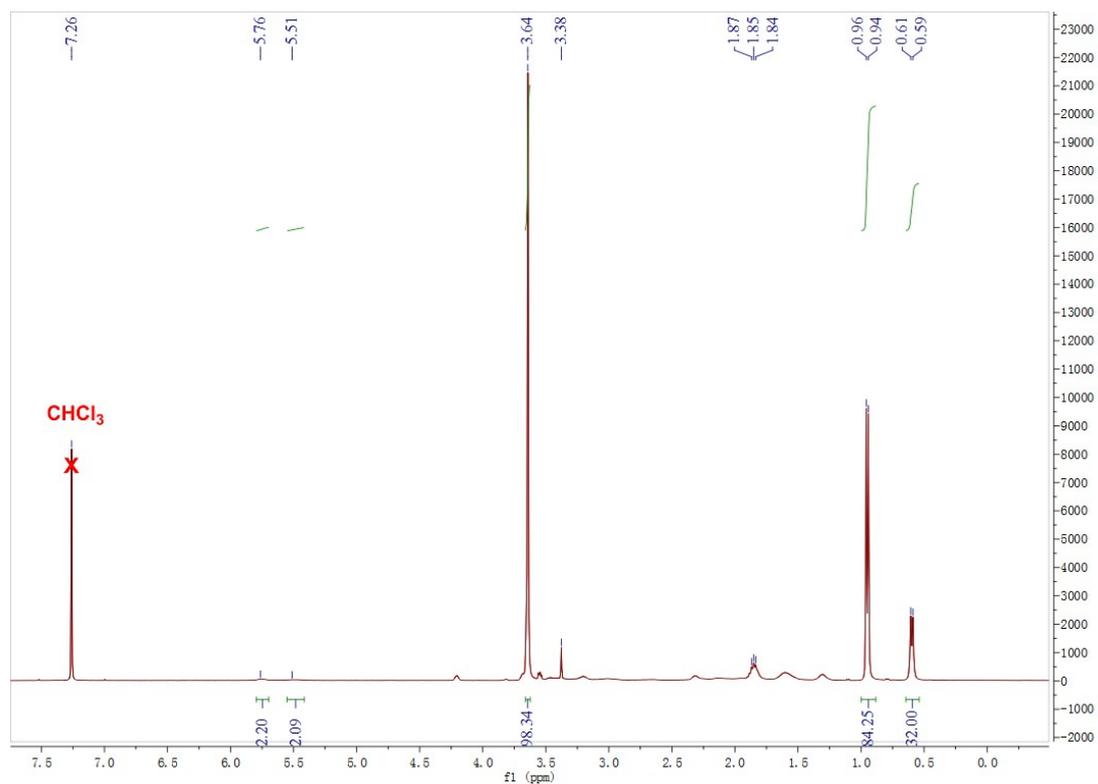


Fig. S32 ^1H NMR spectrum of poly(Norb-2POSS)₂₀-*b*-poly(Norb-PEO)₂₀.

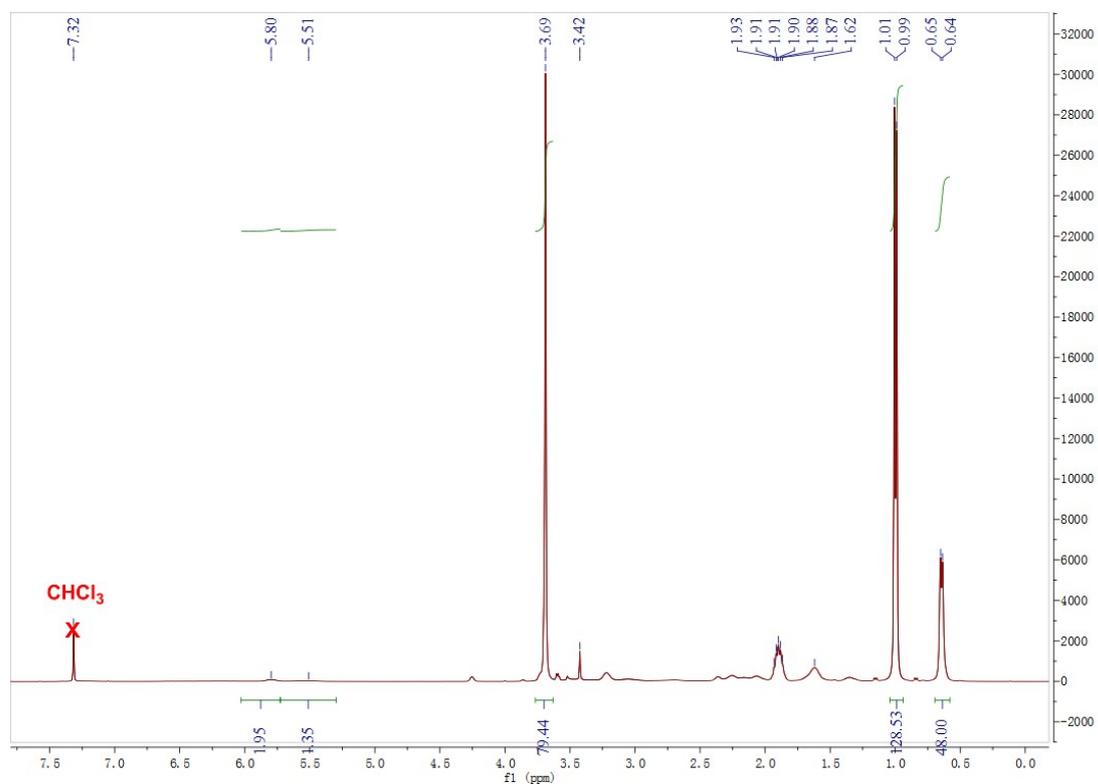


Fig. S33 ^1H NMR spectrum of poly(Norb-3POSS)₂₀-*b*-poly(Norb-PEO)₂₀.

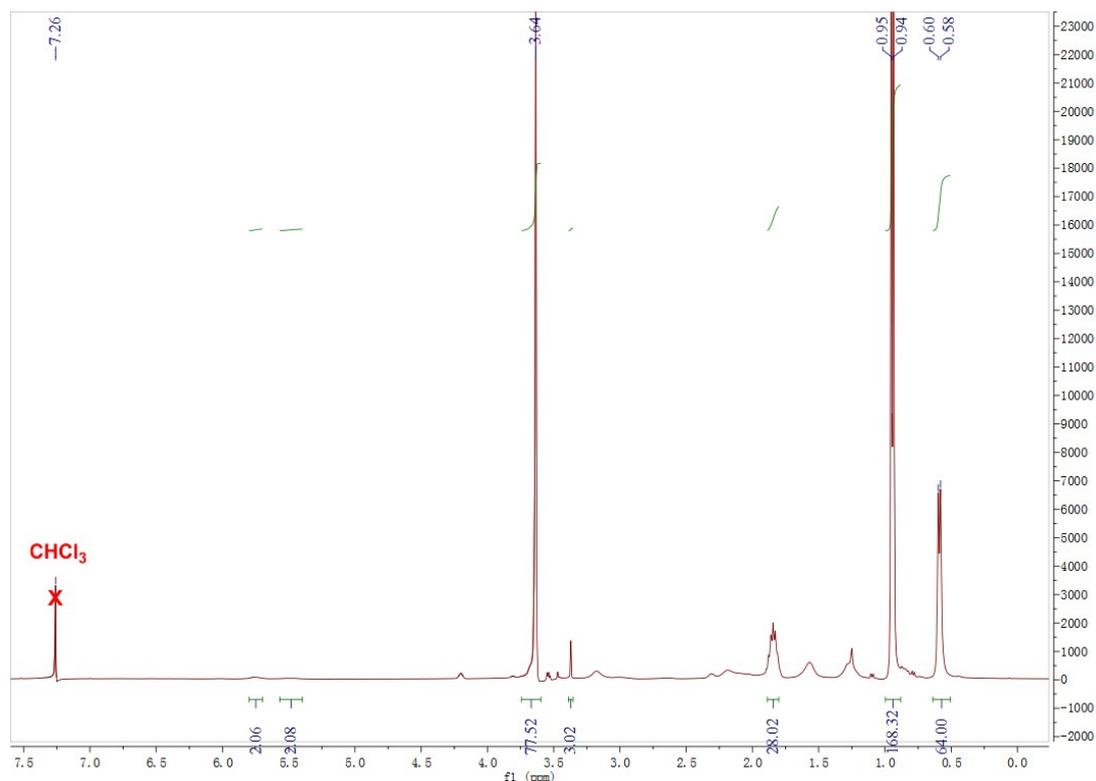


Fig. S34 ^1H NMR spectrum of poly(Norb-4POSS)₂₀-*b*-poly(Norb-PEO)₂₀.

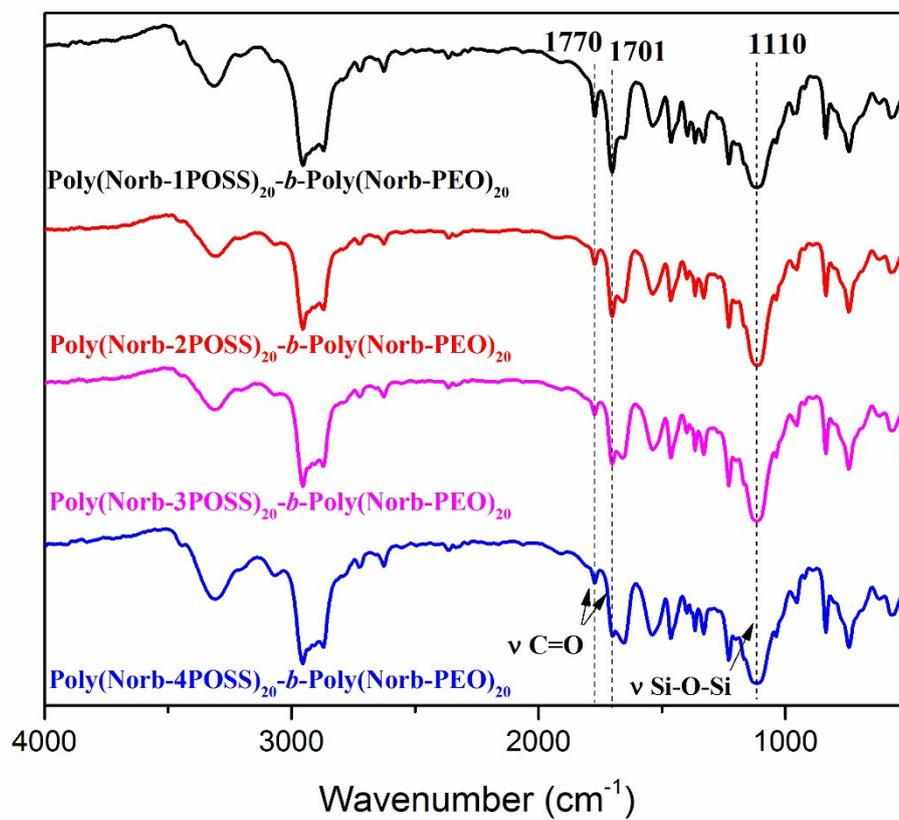


Fig. S35 FT-IR spectra of poly(Norb-*m*POSS)₂₀-*b*-poly(Norb-PEO)₂₀.

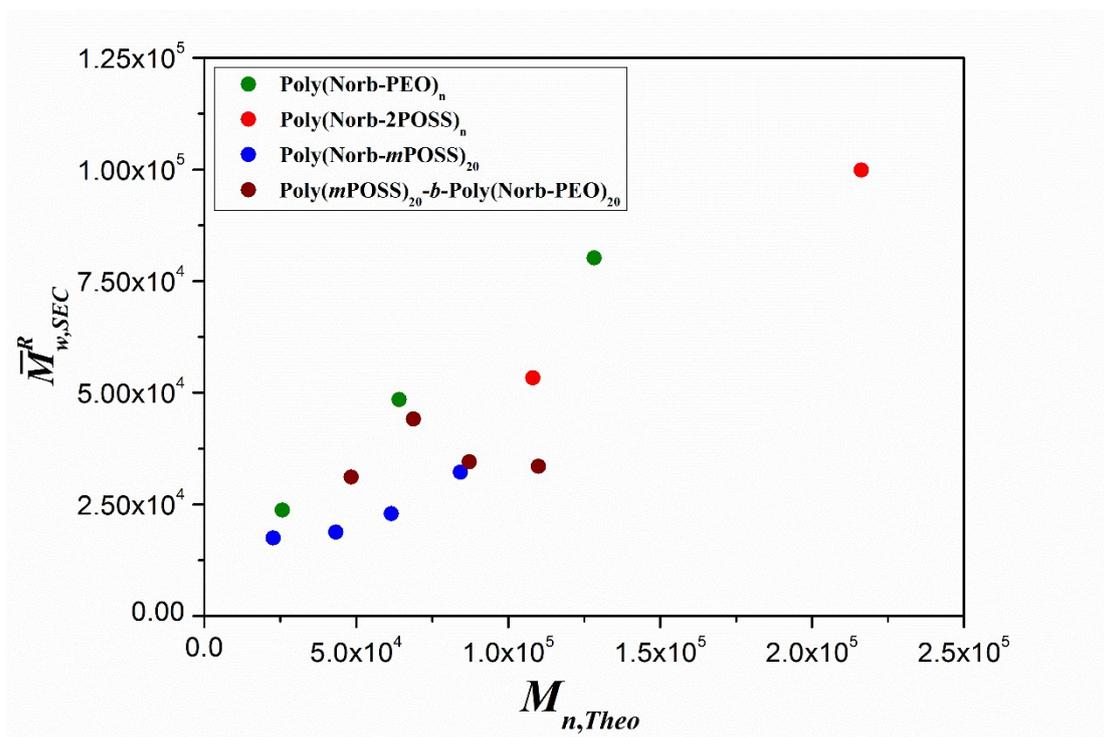


Fig. S36 Plots of $\overline{M}_{w,SEC}^R$ versus $M_{n,Theo}$.

References

1. J. A. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2002, 41, 4035-4037.