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Supporting Information

POSS-based Starlike Hybrid Helical Poly(phenyl isocyanide)s: Synthesis, Self-Assembly, and Their Enantioselective Crystallization Ability

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General consideration

All the ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 400 MHz or 600 MHz spectrometer operated in the Fourier Transform mode. Chemical shifts were reported in delta (δ) units and expressed in parts per million (ppm) downfield with tetramethylsilane as an internal standard. The Fourier transform infrared (FT-IR) spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets at 25 ℃. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear TSK gel GMHHR-H columns. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) data were reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. UV-vis and circular dichroism (CD) spectra were performed on UNIC 4802 UV/vis double beam and JASCO J1500 spectrophotometers, respectively. Quartz cells with 10.0 or 1.0 mm lengths were used in UV-vis and CD measurements. The temperature of the water-jacketed cell holder was controlled by a programmable circulation bath. Transmission electron microscopy (TEM) observations were conducted on a JEM-2100F electron microscope operating at an acceleration voltage of 200 kV. The samples for TEM observation were prepared by casting the corresponding solutions of polymers onto copper mesh grids and drying in air at room temperature. Dynamic light scattering (DLS) measurements were carried on a Nano-ZS90 Zetasizer of Malvern (UK) instrument, and all data were averaged over three time measurements. Fluorescence spectra (FL) were recorded using a Hitachi F-4600 fluorescence spectrophotometer. The slit widths were set at 5.0 nm for both excitation and emission.

All solvents were purchased from Sonopharm Co. Ltd., and were purified by standard procedure before used. All chemicals were obtained from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The POSS-Pd(II) complex, Phenyl isocyanide monomers **1**, **2L**, **2D**, **3** and **4** were prepared according to the reported literatures[1-3] and the structures were confirmed by ^{1}H NMR. All the polymerizations were carried out under a dry nitrogen atmosphere.

Synthesis of POSS-NH$_2$. POSS-NH$_2$ was synthesized according to the literature with modifications.[4] To a 2 L round flask equipped with a magnetic stir bar was added a solution of (3-aminopropyl)triethoxysilane (150 mL, 139.40 g, 0.64 mol) and concentrated HCl (200 mL) in MeOH (1 L). Product started to crystallize after 2 weeks at room temperature. After the solution was stirred for 4 weeks at 25°C, compound was obtained by filtering the reaction mixture, washing with cold MeOH, and drying under vacuum in 45% yield (42.3 g). ^{1}H NMR (600 MHz, DMSO-d_6, 25 °C): δ (ppm) = 8.21 (s, 24H, N$\boldsymbol{H}_3^+$), 2.80 (t, 16H, C$\boldsymbol{H}_2$NH$_3^+$), 1.73 (m, 16H, SiCH$_2$C$\boldsymbol{H}_2$CH$_2$NH$_3^+$), 0.75 (t, 16H, SiC$\boldsymbol{H}_2$); ^{13}C NMR (150 MHz, DMSO-d_6, 25 °C): δ (ppm) = 41.39, 20.99, 8.82. ^{29}Si NMR (DMSO-d_6, 25 °C): δ (ppm) = -66.51. FT-IR (KBr, 25 °C, cm^{-1}): 3041 ($\nu_{\mathrm{N-H}}$), 2935 ($\nu_{\mathrm{C-H}}$), 2872 ($\nu_{\mathrm{C-H}}$), 1615 ($\nu_{\mathrm{NH_3}}$), 1500 ($\nu_{\mathrm{C-N}}$), 1237 ($\nu_{\mathrm{Si-C}}$), 1116 ($\nu_{\mathrm{Si-O-Si}}$), 941 ($\nu_{\mathrm{Si-O-Si}}$), 798 ($\nu_{\mathrm{Si-C}}$), 701 ($\nu_{\mathrm{O-Si-O}}$).

Synthesis of POSS-Alkynyl. To a solution of POSS-NH_2 (0.20 g, 0.17 mmol) in anhydrous dichloromethane was added propargyl 3-carboxylicpropanoate (0.64 g, 4.09 mmol), HBTU (2 equiv with respect to the amino group, 1.30 g, 2.72 mmol), HOBT (2 equiv with respect to the amino group, 0.40 g, 2.72 mmol) and anhydrous triethylamide (2 mL, 16.32 mmol). The reaction was allowed to proceed in N_2 atmosphere for 3 days at room temperature. After the solvent was removed by evaporation under reduced pressure, the residue was dissolved in CH_2Cl_2, washed with saturated $NaHCO_3$, $NaHSO_4$, and NaCl solution several times. The crude product containing solution was dried with Na_2SO_4 and then concentrated and recrystallized in cold diethyl ether, and a white solid (POSS-Alkynyl) was obtained, 83% yield (0.28 g). ^1H NMR (600 MHz, $CDCl_3$, 25 °C), δ (ppm) = 6.49 (8H, $N\boldsymbol{H}CO$), 3.21 (16H, $C\boldsymbol{H}_2NH$), 1.59 (16H, $SiCH_2C\boldsymbol{H}_2CH_2NH$), 0.63 (16H, $SiC\boldsymbol{H}_2$), 4.68 (16H, $OC\boldsymbol{H}_2C{\equiv}CH$), 2.71 (16H, $OOCC\boldsymbol{H}_2CH_2COOH$), 2.53 (16H, $OOCCH_2C\boldsymbol{H}_2COOH$), and 2.48 (8H, $CH_2C{\equiv}C\boldsymbol{H}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ (ppm) = 172.26, 171.36, 77.57, 75.02, 52.08, 41.99, 30.63, 29.36, 22.90, 9.01. ^{29}Si NMR ($CDCl_3$, 25 °C): δ (ppm) = -66.84. FT-IR (KBr, 25 °C, cm^{-1}): 3091 ($\nu_{C\text{-}C{\equiv}CH}$) , 3041 ($\nu_{N\text{-}H}$), 2935 ($\nu_{C\text{-}H}$), 2872 ($\nu_{C\text{-}H}$), 1717 ($\nu_{C=O}$), 1500 ($\nu_{C\text{-}N}$),1237 ($\nu_{Si\text{-}C}$), 1116 ($\nu_{Si\text{-}O\text{-}Si}$), 941 ($\nu_{Si\text{-}O\text{-}Si}$), 798 ($\nu_{Si\text{-}C}$), 701 ($\nu_{O\text{-}Si\text{-}O}$).

Synthesis of POSS-Pd(II). To a solution of POSS-Alkynyl (0.10 g, 0.05 mmol) in triethylamide (6 mL) and dichloromethane (6 mL) was added trans-bis(triethylphosphine)palladium(II) dichloride (0.17 g, 0.40 mmol) and copper(I) chloride (4.0 mg, 0.04 mmol). The mixture solution was stirred at room temperature for 2 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by column chromatography with MeOH as eluent. The afforded product was recrystallized from petrol ether and ethyl acetate to give POSS-Pd(II) as a yellow solid, 88% yield (0.22 mg,) ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C), δ (ppm) = 6.54 (8H, N$\boldsymbol{H}$CO), 3.19 (16H, C$\boldsymbol{H}_2$NH), 1.62 (16H, $SiCH_2C\boldsymbol{H}_2CH_2NH$), 0.62 (16H, $SiC\boldsymbol{H}_2$); 4.70 (16H, $OC\boldsymbol{H}_2C{\equiv}CH$), 2.65 (16H, $OOCC\boldsymbol{H}_2CH_2COOH$), 2.49 (16H, $OOCCH_2C\boldsymbol{H}_2COOH$), 1.91 (12H, $PC\boldsymbol{H}_2CH_3$) and 1.16 (18H, $PCH_2C\boldsymbol{H}_3$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ (ppm) = 172.61, 171.48, 60.35, 55.09, 41.97, 30.74, 29.44, 22.94, 15.18, 11.40, 8.27. ^{29}Si NMR ($CDCl_3$, 25 °C): δ (ppm) = -66.97. ^{31}P NMR ($CDCl_3$, 25 °C) δ (ppm) = 17.60. FT-IR (KBr, 25 °C, cm^{-1}): 3041 ($\nu_{N\text{-}H}$), 2935 ($\nu_{C\text{-}H}$), 2872 ($\nu_{C\text{-}H}$), 1717 ($\nu_{C=O}$), 1500 ($\nu_{C\text{-}N}$), 1237 ($\nu_{Si\text{-}C}$), 1116 ($\nu_{Si\text{-}O\text{-}Si}$), 941 ($\nu_{Si\text{-}O\text{-}Si}$), 798 ($\nu_{Si\text{-}C}$), 701 ($\nu_{O\text{-}Si\text{-}O}$).

Typical polymerization procedure for POSS-poly-$\boldsymbol{1_n}$s. The polymerization procedure is given below taking POSS-poly-$\mathbf{1}_{60}$ as an example. A 10 mL oven-dried and nitrogen-filled flask was charged with monomer **1** (137.70 mg, 5.00 mmol), and POSS-Pd(II) (3.00 mg, 0.05 mmol) in THF (2.4 mL), and a stir bar. The concentrations of monomer **1** and catalyst POSS-Pd(II) were 0.2 M and 0.003 M, respectively ($[\mathbf{1}]_0$/[POSS-Pd(II)]$_0$ = 60). The degassed reaction flask was then immersed into a pre-heated oil bath at 55 °C and stirred for 8 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, dried in vacuum at room temperature overnight, afforded POSS-poly-$\mathbf{1}_{60}$ in 88 % yield. SEC: $M_n = 2.13 \times 10^4$ Da, $M_w/M_n = 1.11$. ^{1}H

NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 7.31 (brs, 2H, aromatic), 5.76 (brs, 2H, aromatic), 4.08-3.79 (brs, 2H, OC$\boldsymbol{H}_2$), 1.51-0.84 (brs, 19H, C$\boldsymbol{H}_2$ and C$\boldsymbol{H}_3$). FT-IR (KBr, 25 °C, cm^{-1}): 3041 (ν_{N-H}), 2935 (ν_{C-H}), 2872 (ν_{C-H}), 1717 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$), 1500 (ν_{C-N}), 1237 (ν_{Si-C}), 1116 ($\nu_{Si-O-Si}$), 941 ($\nu_{Si-O-Si}$), 798 (ν_{Si-C}), 701 (ν_{O-Si-O}).

Typical polymerization procedure for POSS-poly-2L$_n$s. The polymerization procedure is given below taking POSS-poly-$\mathbf{2L}_{60}$ as an example. This hybrid polymer was prepared in 87% yield under the same procedure to that of POSS-poly-$\mathbf{1}_{60}$ by using monomer **2L**. SEC: $M_n = 2.42 \times 10^4$ Da, $M_w/M_n = 1.16$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.82-8.29 (brs, 1H, N$\boldsymbol{H}$), 6.94-5.12 (brs, 4H, aromatic), 4.89-4.40 (brs, H, C$\boldsymbol{H}$), 4.34-3.72 (brs, 2H, C$\boldsymbol{H}_2$), 1.62-1.30 (brs, 19H, C$\boldsymbol{H}_2$ and C$\boldsymbol{H}_3$), 1.12-0.88 (brs, 3H, C$\boldsymbol{H}_3$). FT-IR (KBr, 25 °C, cm^{-1}): 3041 (ν_{N-H}), 2935 (ν_{C-H}), 2872 (ν_{C-H}), 1717 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$), 1500 (ν_{C-N}), 1237 (ν_{Si-C}), 1116 ($\nu_{Si-O-Si}$), 941 ($\nu_{Si-O-Si}$), 798 (ν_{Si-C}), 701 (ν_{O-Si-O}).

Synthesis of POSS-poly-2D$_{100}$. This hybrid polymer POSS-poly-$\mathbf{2D}_{100}$ was prepared in 85% yield under the same procedure to that of POSS-poly-$\mathbf{1}_{60}$ by using monomer **2D**. SEC: $M_n = 2.45 \times 10^4$ Da, $M_w/M_n = 1.17$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) =8.82-8.29 (brs, 1H, N$\boldsymbol{H}$), 6.94-5.12 (brs, 4H, aromatic), 4.89-4.40 (brs, H, C$\boldsymbol{H}$), 4.34-3.72 (brs, 2H, C$\boldsymbol{H}_2$), 1.62-1.30 (brs, 19H, C$\boldsymbol{H}_2$ and C$\boldsymbol{H}_3$), 1.12-0.88 (brs, 3H, C$\boldsymbol{H}_3$). FT-IR (KBr, 25 °C, cm^{-1}): 3041 (ν_{N-H}), 2935 (ν_{C-H}), 2872 (ν_{C-H}), 1717 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$), 1500 (ν_{C-N}), 1237 (ν_{Si-C}), 1116 ($\nu_{Si-O-Si}$), 941 ($\nu_{Si-O-Si}$), 798 (ν_{Si-C}), 701 (ν_{O-Si-O}).

Typical polymerization procedure for POSS-poly(2L$_{20}$-b-3$_m$)s. The polymerization procedure is given below taking POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) as an example. Into a 10 mL reaction tube with magnetic stirring bar was added POSS-poly-**2L**$_{20}$ (40.0 mg, 6.63×10^{-4} mmol), monomer **3** (76.9 mg, 0.106 mmol) and dry THF (1.2 mL) under nitrogen. The reaction solution was kept stirring for 18 h at 55 °C. After that, the mixture was precipitated into a large amount of methanol, and the precipitated solid was collected by centrifugation. The isolated POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) was washed with methanol several times. After dried in vacuum at room temperature overnight, POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) was obtained as a brown solid (88% yield). SEC: $M_n = 2.44 \times 10^4$ Da, $M_w / M_n = 1.21$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.05-7.36 (br, Ar$\boldsymbol{H}$ and N$\boldsymbol{H}$), 6.94-5.98 (brs, 4H, aromatic and phenyl isocyanide monomer **3**), 5.30-5.18 (br, $C\boldsymbol{H}_2$ of phenyl isocyanide repeating units), 4.17-3.37 (br, $C\boldsymbol{H}$ and $CO_2C\boldsymbol{H}_2$, $OC\boldsymbol{H}_2$ and $OC\boldsymbol{H}_3$ of TEG chains), 1.62-1.30 (brs, 19H, $C\boldsymbol{H}_2$ and $C\boldsymbol{H}_3$), 1.12-0.99 (brs, 3H, $C\boldsymbol{H}_3$). FT-IR (KBr, 25 °C, cm^{-1}): 3041 ($\nu_{N\text{-}H}$), 2935 ($\nu_{C\text{-}H}$), 2872 ($\nu_{C\text{-}H}$), 1717 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$), 1500 ($\nu_{C\text{-}N}$), 1237 ($\nu_{Si\text{-}C}$), 1116 ($\nu_{Si\text{-}O\text{-}Si}$), 1099($\nu_{C\text{-}O}$), 941 ($\nu_{Si\text{-}O\text{-}Si}$), 798 ($\nu_{Si\text{-}C}$), 701 ($\nu_{O\text{-}Si\text{-}O}$).

Self-assembly of amphiphilic POSS-poly(2L$_{20}$-b-3$_m$)s copolymers in aqueous solutions. The self-assembly of POSS-poly(**2L**$_{20}$-*b*-**3**$_m$)s copolymers was conducted by dissolving the copolymer in THF and then dialyzing against deionized water. Taking POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) as an example, 10 mg of the copolymer was firstly dissolved in 10 mL of THF. Then, deionized water was added into the solution at a rate of 1 mL/h under vigorous stirring until the solution changed from transparent to translucent. Then the solution was subsequently dialyzed against deionized water for 72 h (dialysis membrane, molecular weight cut-off:14000 g/mol) at room temperature. After being diluted with deionized water and equilibrated at room temperature for 48 h, the self-assemblies of POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) in aqueous solutions were obtained.

Critical aggregation concentration (CAC) measurement of POSS-poly(2L$_{20}$-b-3$_{m}$)s copolymers. The CACs of POSS-poly(**2L**$_{20}$-*b*-**3**$_{m}$)s copolymers in aqueous solutions were measured using pyrene as a fluorescent probe. Taking POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) as an example, the CAC measurement for POSS-poly(**2L**$_{20}$-*b*-**3**$_{m}$)s was performed as follows. Pyrene (5.1 mg) was dissolved in 15 mL of acetone and then 10 μL of the solution was added into each cuvette. The acetone was allowed to evaporate. Then 2.0 mL of POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$) aqueous solutions with concentrations ranging from 0.976 to 500 mg/L were added into the pyrene-containing cuvette separately. Upon sonication for 10 min, the solutions were kept at room temperature and equilibrated for 24 h before fluorescent emission measurements with an excitation wavelength of 335 nm. The emission spectra were recorded in the 340-600 nm wavelength range. For each spectrum obtained, the intensity ratio of the first and third peaks, I_1/I_3, was calculated. The CAC was estimated as the concentration at which I_1/I_3 began to drop, indicating that polymer aggregation occurred.

Typical polymerization procedure for POSS-poly(2L$_{n}$-b-4$_{m}$)s. The polymerization procedure is given below taking POSS-poly(**2L**$_{100}$-*b*-**4**$_{5}$) as an example. Into a 10 mL reaction tube with magnetic stirring bar was added POSS-poly-**2L**$_{100}$ (60.0 mg, 1.99×10^{-4} mmol), monomer **4** (2.5 mg, 0.008 mmol) and dry THF (1.2 mL) under nitrogen. The reaction solution was kept stirring for 12 h at 55 °C. After that, the mixture was precipitated into a large amount of methanol, and the precipitated solid was collected by centrifugation. The isolated POSS-poly(**2L**$_{100}$-*b*-**4**$_5$) was washed with methanol several times. After dried in vacuum at room temperature overnight, POSS-poly(**2L**$_{100}$-*b*-**4**$_5$) was obtained as a brown solid (80% yield). SEC: $M_n = 3.68\times10^4$, $M_w/M_n = 1.19$. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ (ppm) = 8.82-8.28 (brs, 1H, N***H***), 6.94-5.8 (brs, 4H, aromatic), 5.37-5.12(brs, H, C***H***), 4.47-3.05 (brs, 2H, C***H***$_2$), 1.62-1.25 (brs, 19H, C***H***$_2$ and C***H***$_3$), 0.45-1.12 (brs, 3H, C***H***$_3$). ^{19}F NMR (CDCl$_3$, 25 °C): δ (ppm) = -153.03, -156.96, -162.37. FT-IR (KBr, 25 °C, cm^{-1}): 3041 ($\nu_{N\text{-}H}$), 2935 ($\nu_{C\text{-}H}$), 2872 ($\nu_{C\text{-}H}$), 1717 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$), 1500 ($\nu_{C\text{-}N}$), 1237 ($\nu_{Si\text{-}C}$), 1116 ($\nu_{Si\text{-}O\text{-}Si}$), 941 ($\nu_{Si\text{-}O\text{-}Si}$), 798 ($\nu_{Si\text{-}C}$), 701 ($\nu_{O\text{-}Si\text{-}O}$).

Synthesis of the Cross-Linked Hybrid Helical Polymer. A 10 mL oven dried and nitrogen-filled flask was charged with POSS-poly(**2L**$_{100}$-*b*-**4**$_5$) (100.0 mg, $M_n = 3.68\times10^4$, $M_w/M_n = 1.19$), cystamine (12 mg, 0.08 mmol), dry THF (2.0 mL), triethylamide (2.0 mL), and a stir bar. The reaction flask was then immersed into an oil bath at 55 °C and stirred for 12 h. After cooled to room temperature, cross-linked hybrid helical polymer was obtained by washing with THF and drying under vacuum at room temperature (68 % yield).

References

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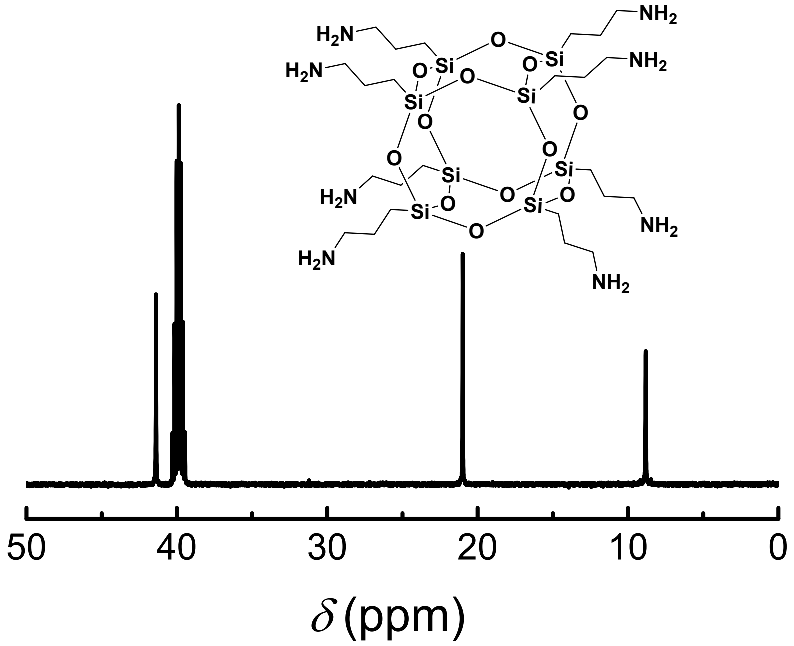

Fig. S1 ^{13}C NMR spectrum of POSS-NH_2 measured in DMSO-d_6 at 25 °C.

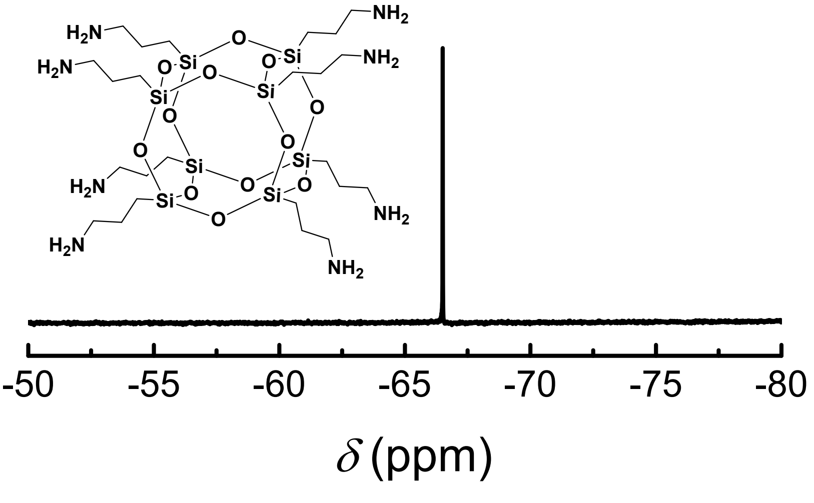

Fig. S2 ^{29}Si NMR spectrum of POSS-NH_2 measured in DMSO-d_6 at 25 °C.

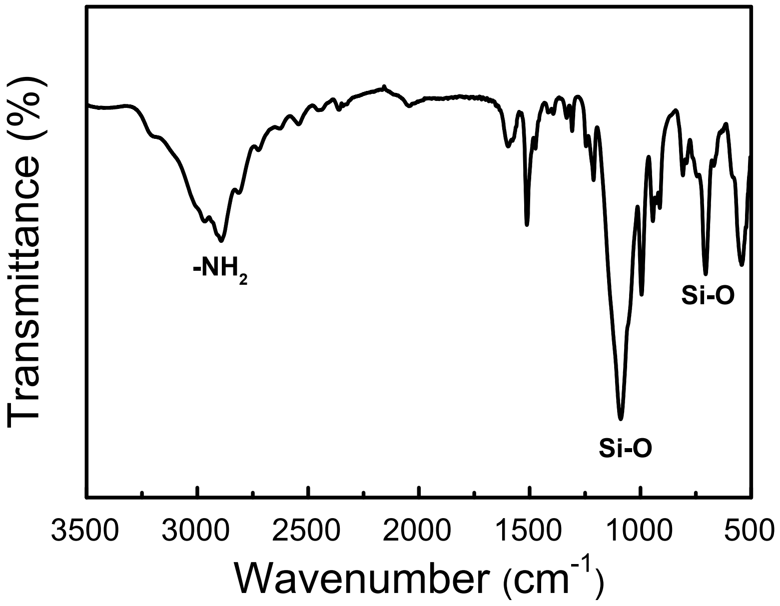

Fig. S3 FT-IR spectrum of POSS-NH$_2$ measured at 25 °C using KBr pellet.

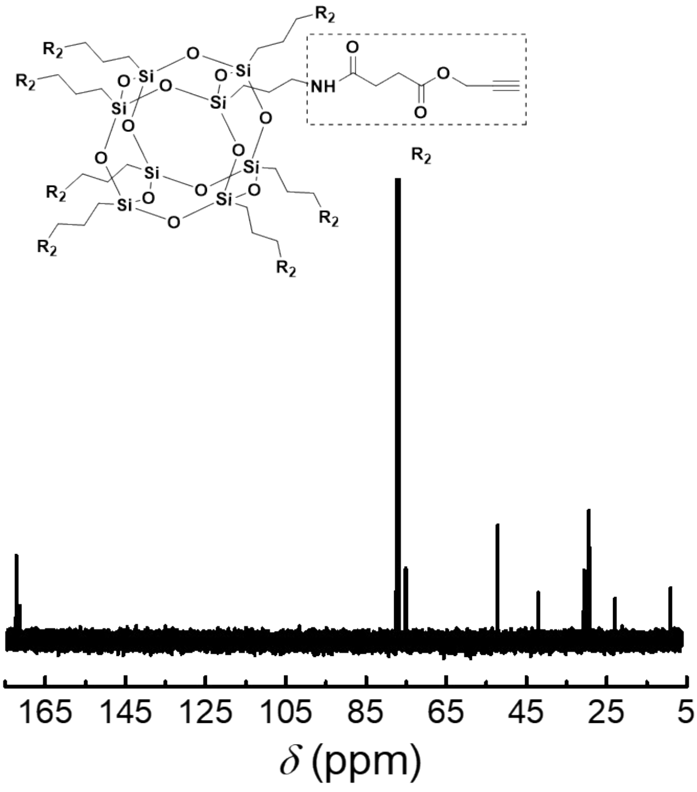

Fig. S4 ^{13}C NMR spectrum of POSS-Alkynyl measured in CDCl$_3$ at 25 °C.

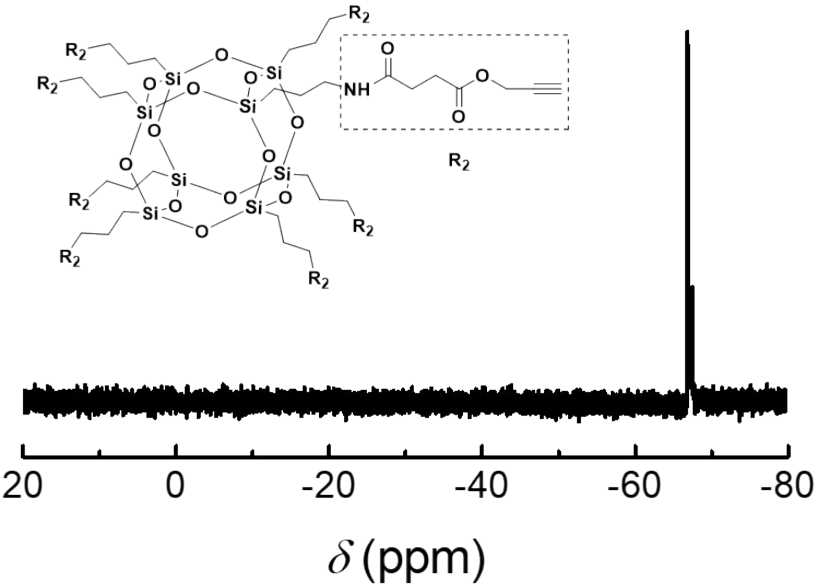

Fig. S5 ^{29}Si NMR spectrum of POSS-Alkynyl measured in $CDCl_3$ at 25 °C.

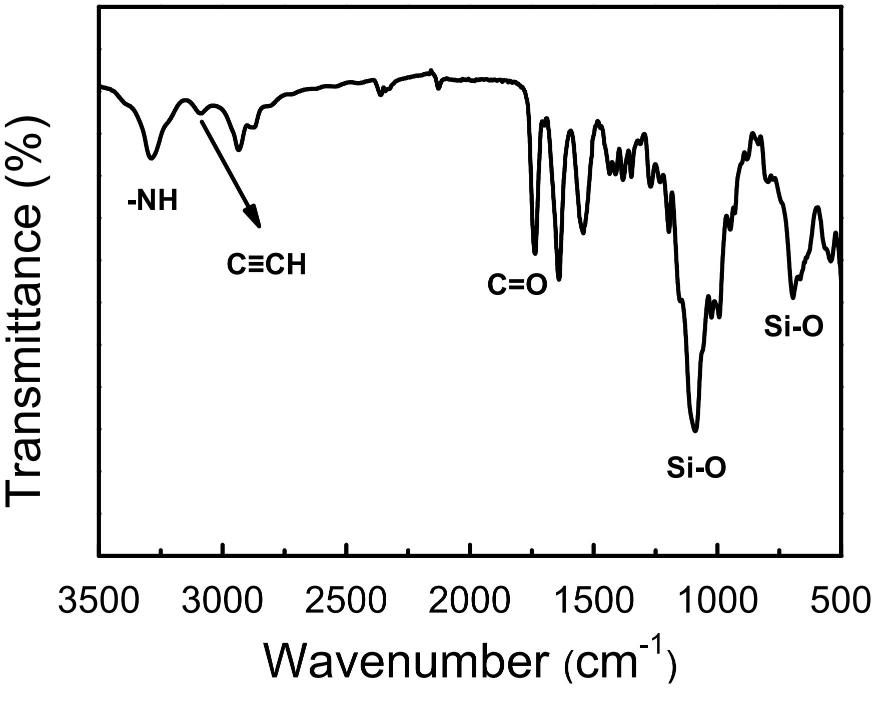

Fig. S6 FT-IR spectrum of POSS-Alkynyl measured at 25 °C using KBr pellet.

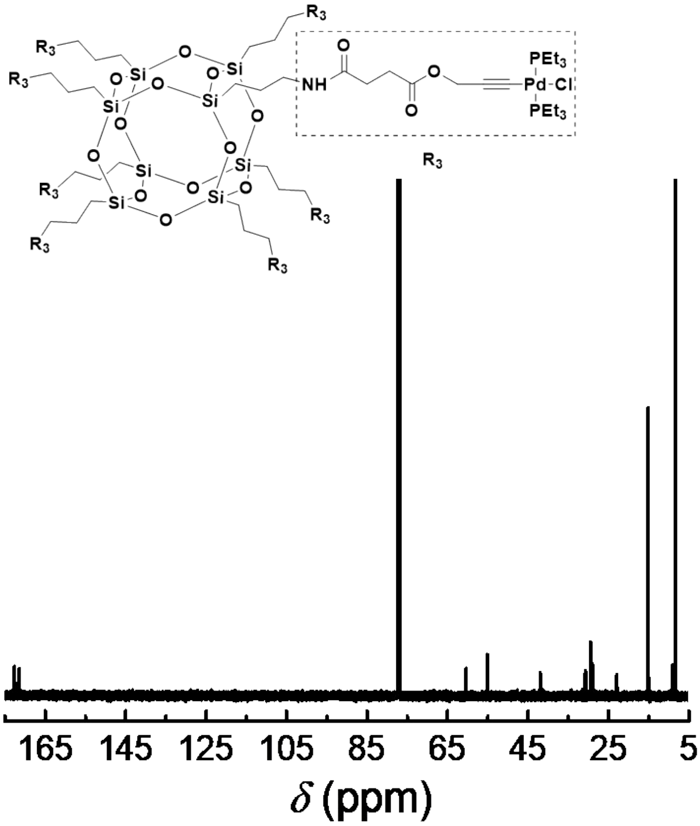

Fig. S7 ^{13}C NMR spectrum of POSS-Pd(II) measured in $CDCl_3$ at 25 °C.

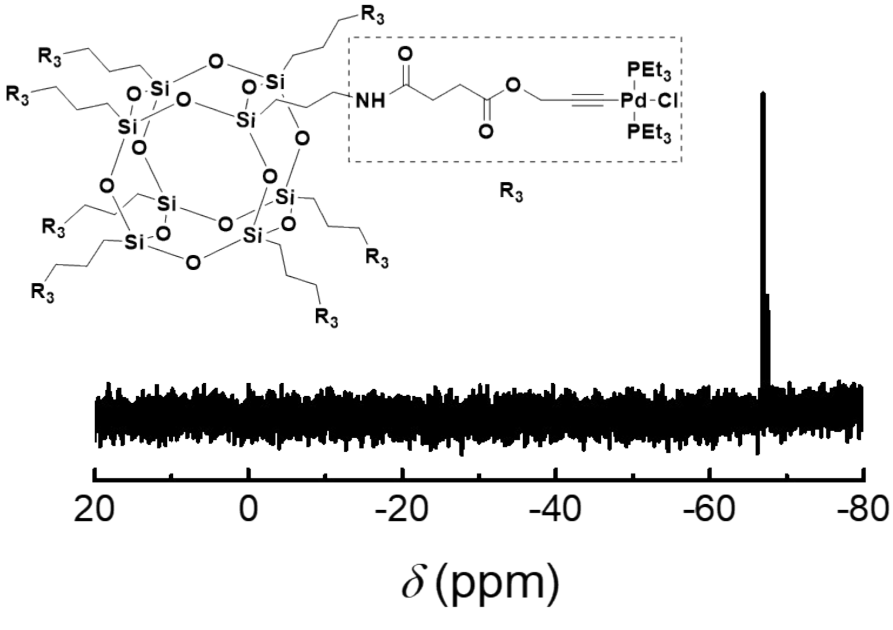

Fig. S8 ^{29}Si NMR spectrum of POSS-Pd(II) measured in $CDCl_3$ at 25 °C.

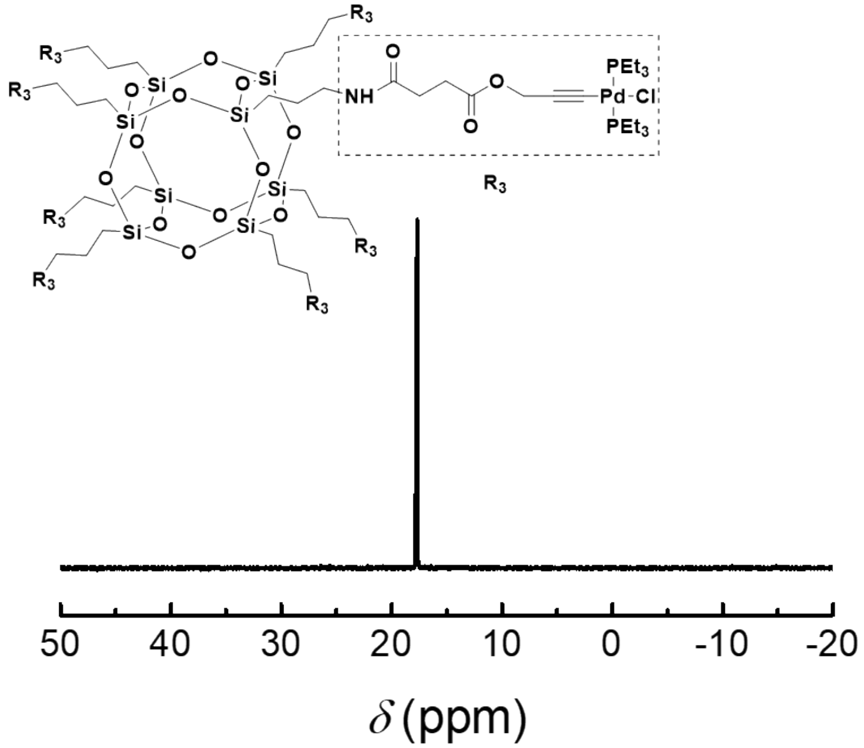

Fig. S9 ^{31}P NMR spectrum of POSS-Pd(II) measured in $CDCl_3$ at 25 °C.

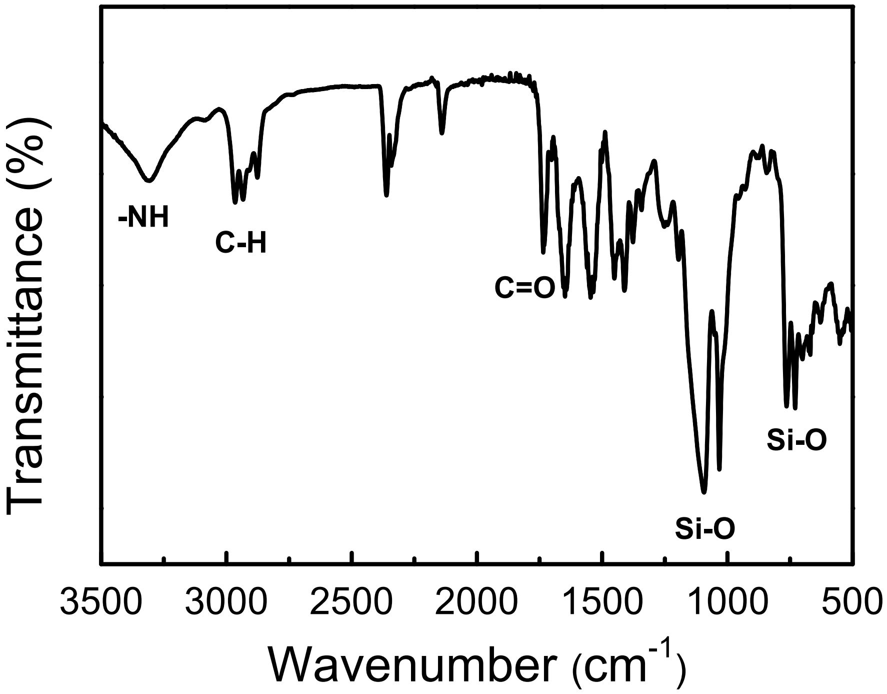

Fig. S10 FT-IR spectrum of POSS-Pd(II) measured at 25 °C using KBr pellet.

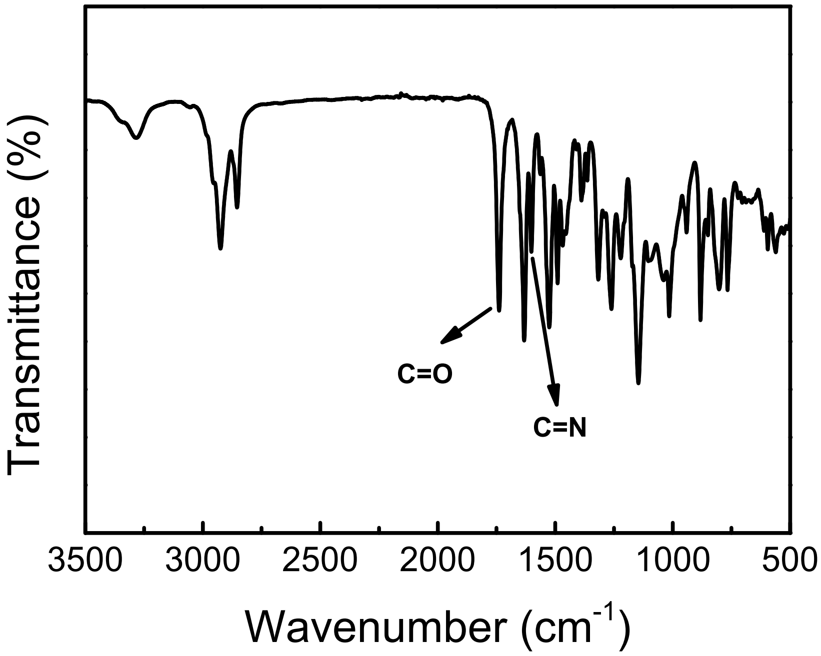

Fig. S11 FT-IR spectrum of POSS-poly-$\mathbf{1}_{60}$ measured at 25 ℃ using KBr pellet.

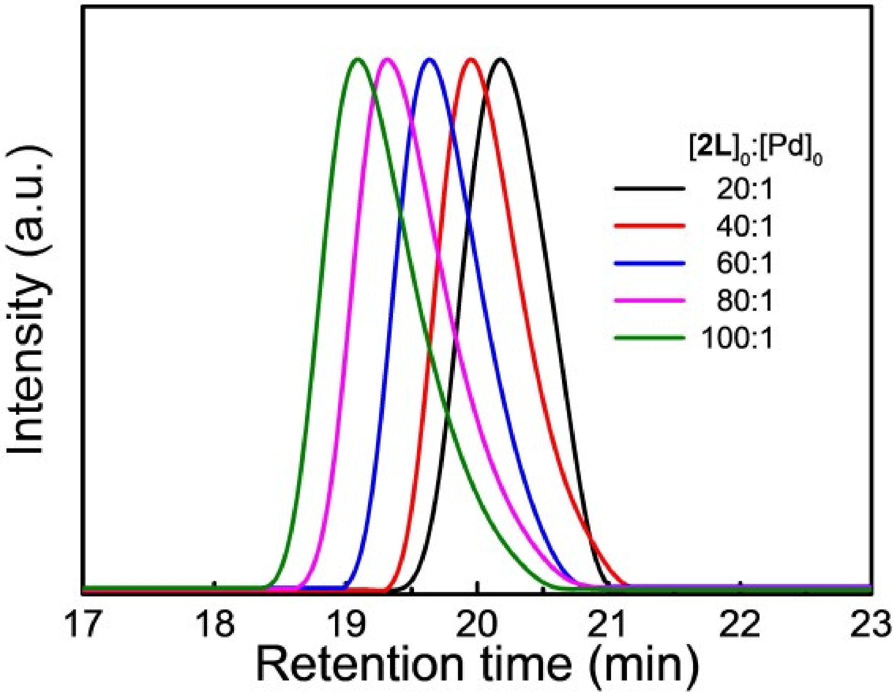

Fig. S12 SEC curves of POSS-poly-$\mathbf{2L}_n$s synthesized by the polymerization of the monomer **2L** initiated by POSS-Pd(II) in THF at 55 °C under different feed ratios of **2L** to POSS-Pd(II).

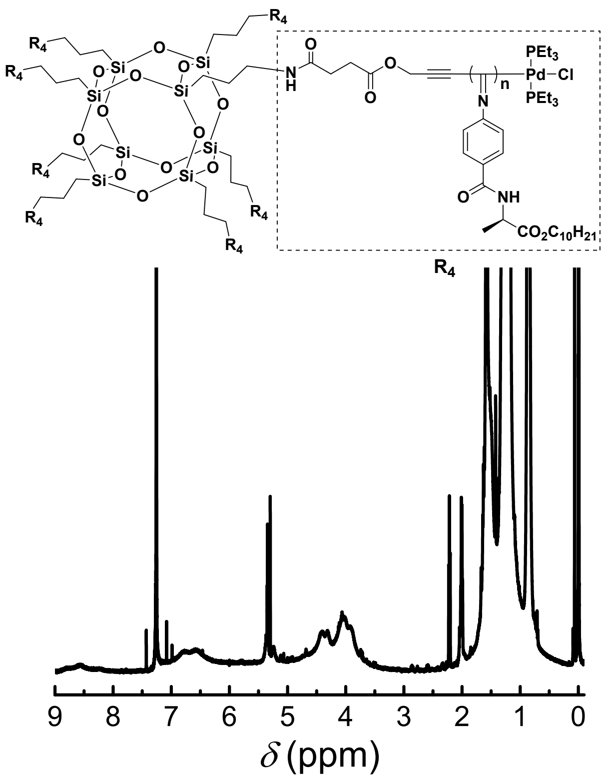

Fig. S13 ^{1}H NMR spectrum of POSS-poly-**2L**$_{60}$ measured in $CDCl_3$ at 25 °C.

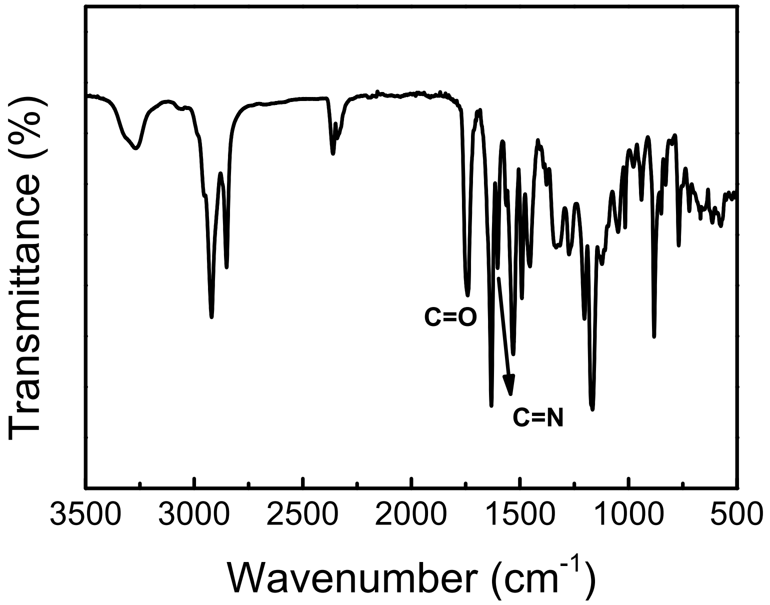

Fig. S14 FT-IR spectrum of POSS-poly-**2L**$_{60}$ measured at 25 °C using KBr pellet.

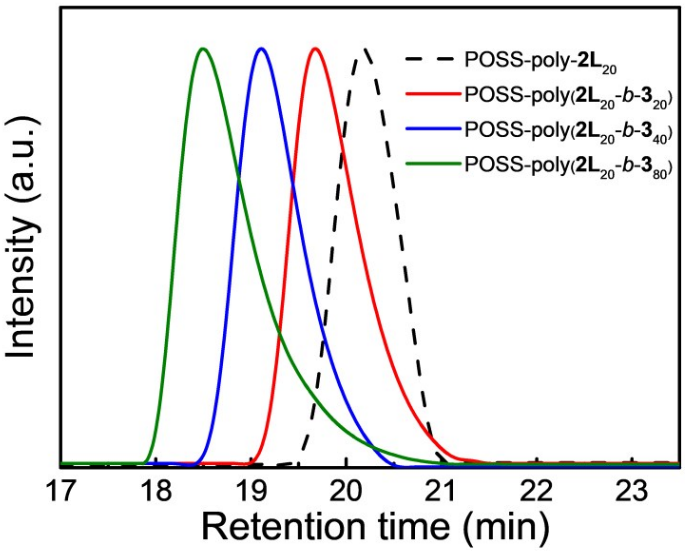

Fig. S15 SEC curves of POSS-poly-$\mathbf{2L}_{20}$-b-$\mathbf{3}_{\mathrm{m}}$ prepared from the polymerization of the monomer **3** in THF at 55 °C using POSS-poly-$\mathbf{2L}_{20}$ as the initiator.

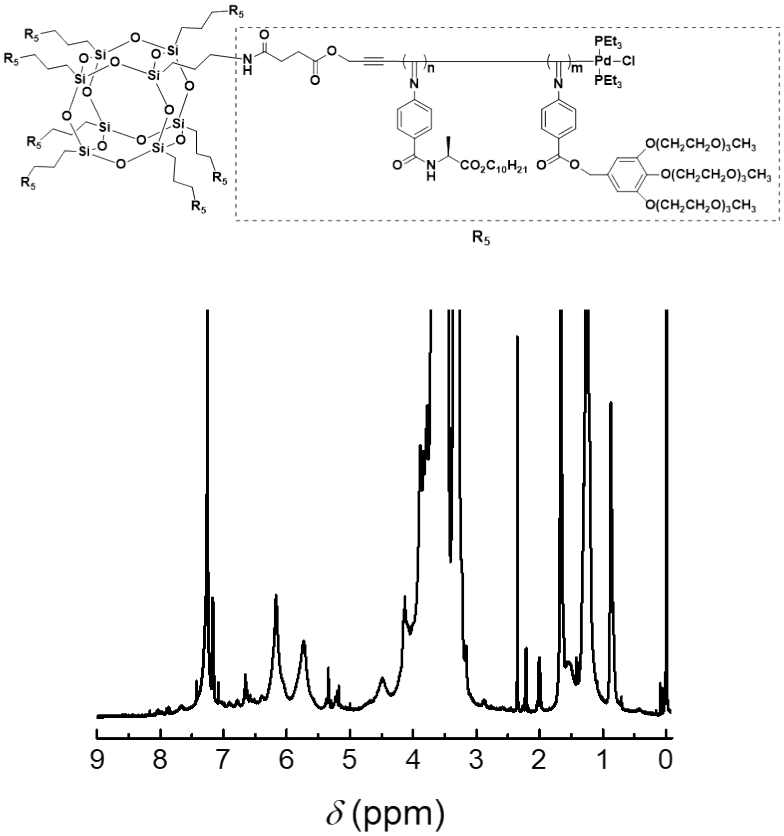

Fig. S16 ^{1}H NMR spectrum of POSS-poly($\mathbf{2L}_{20}$-b-$\mathbf{3}_{20}$) measured in $CDCl_3$ at 25 °C.

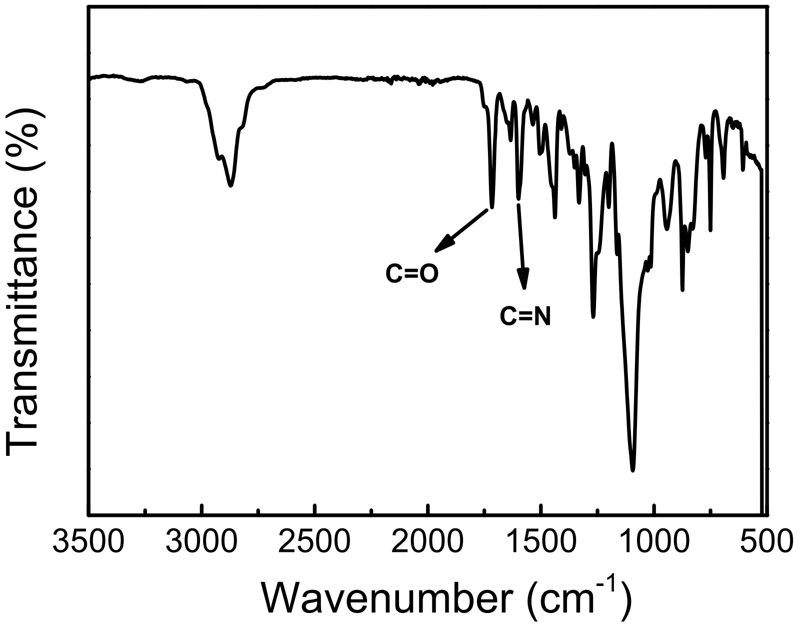

Fig. S17 FT-IR spectrum of POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$**)** measured in $CDCl_3$ at 25 ℃ using KBr pellet.

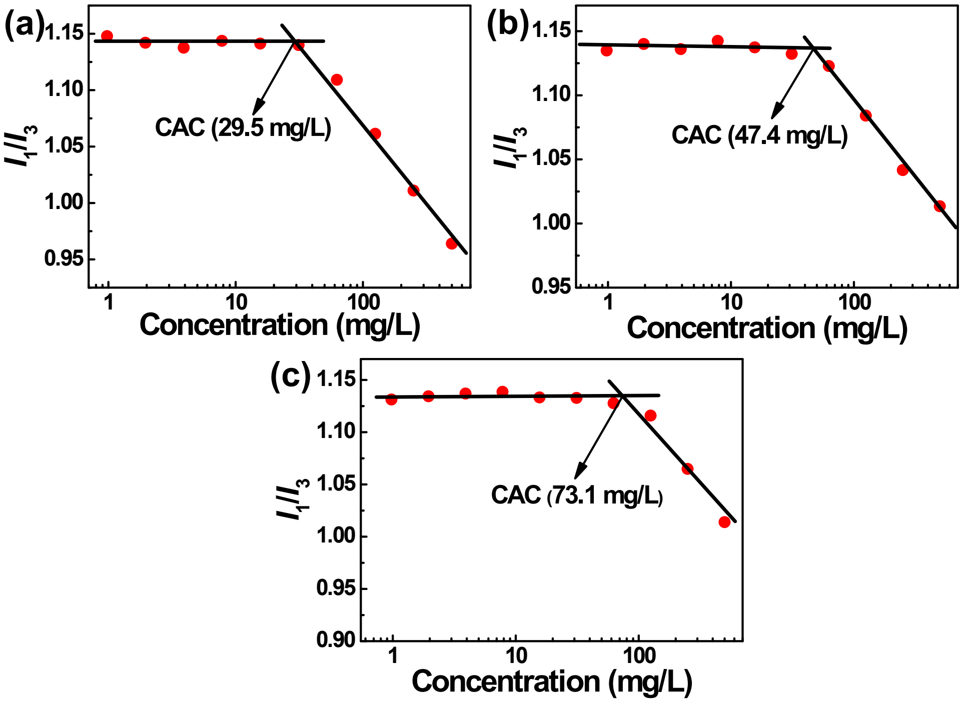

Fig. S18 CAC of the (a) POSS-poly(**2L**$_{20}$-*b*-**3**$_{20}$), (b) POSS-poly(**2L**$_{20}$-*b*-**3**$_{40}$), and (c) POSS-poly(**2L**$_{20}$-*b*-**3**$_{80}$).

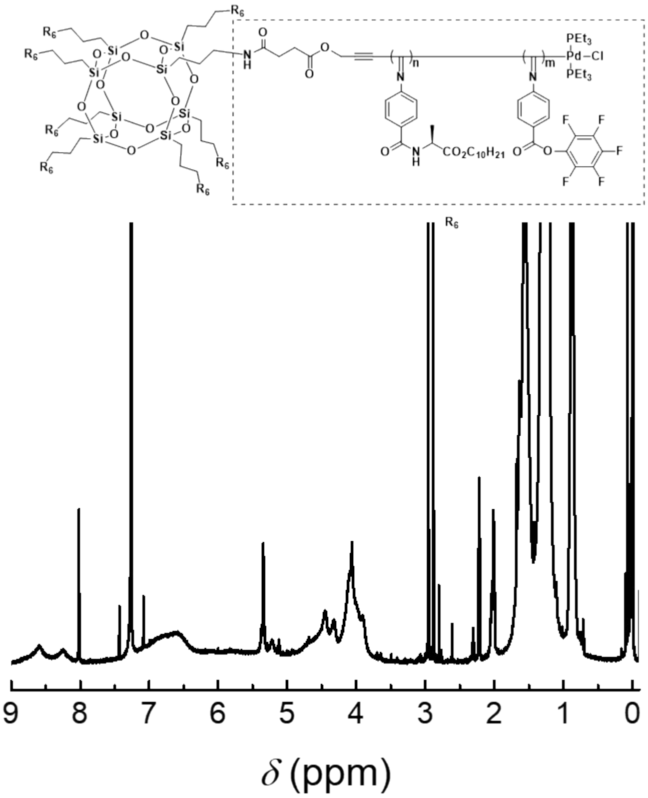

Fig. S19 ^{1}H NMR spectrum of POSS-poly(**2L**$_{100}$-*b*-**4**$_5$) measured in CDCl$_3$ at 25 ℃.

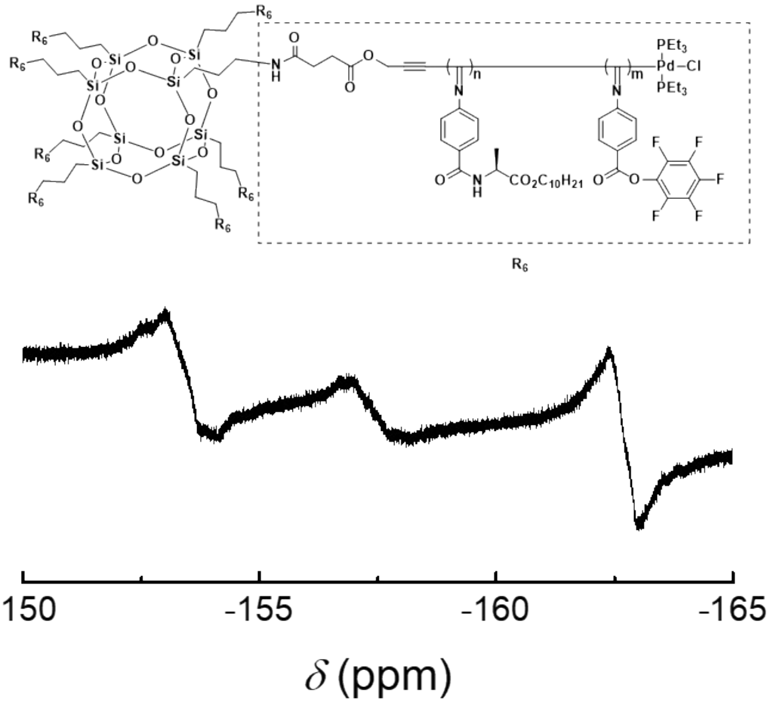

Fig. S20 ^{19}F NMR spectrum of POSS-poly(**2L$_{100}$**-*b*-**4**$_5$) measured in CDCl$_3$ at 25 ℃.

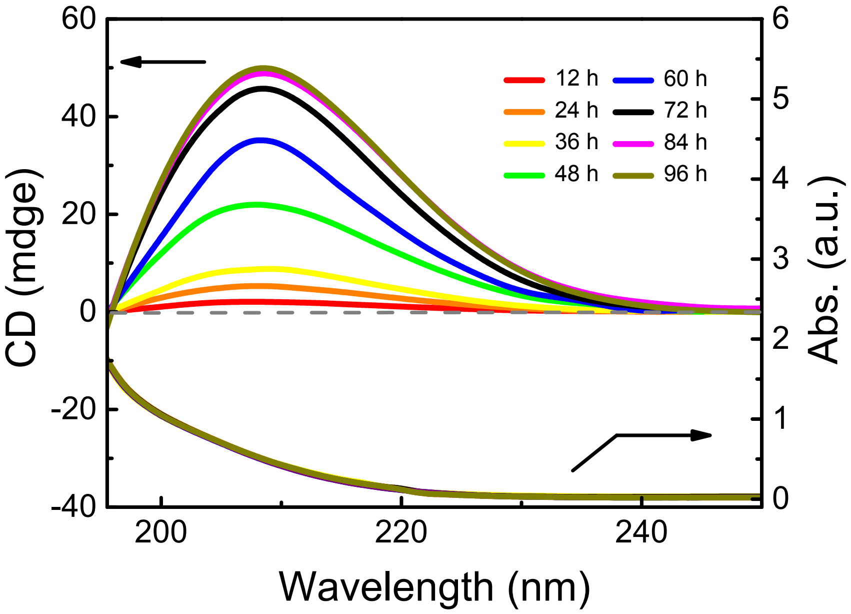

Fig. S21 Time-dependent CD and UV-vis absorption spectra for the enantioselective crystallization of racemic threonine in aqueous solutions induced by cross-linked POSS-poly-$\mathbf{2L}_{100}$ at room temperature.