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Supporting Information

A New Route to Achieve Side-Chain-Type Sulfone-Containing Polysiloxanes via Sulfide Oxidation-Induced Cleavage and Rearrangement of Si–O–Si Bonds with Fine Selectivity Toward Cyclosiloxanes

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Experimental

Materials

2,2–Dimethoxy–2–phenylacetophenone (DMPA) and Oxone® were purchased from Aladdin Co. (China) and used as received. Tetramethyltetravinylcyclotetrasiloxane (D_4^{Vi}) was obtained as commercial products and used directly. Ethyl mercaptan and Methyl-mercaptopropionate were provided by Sigma–Aldrich and used as received. Tetrahydrofuran (THF) was purified according to routine procedure and distilled over sodium before use. Octavinylsilsesquioxane (OVS) was synthesized using the classic procedure.

Characterization and measurements

The reaction was irradiated by UV on a Spectroline Model SB–100P/FA lamp (365 nm, 100 w). UV intensity is 4500μW/cm ^{2} at a distance of 38 cm. Proton nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{29}Si NMR) spectra were recorded on a Bruker AVANCE 400 spectrometer at 25 °C using $CDCl_3$ as solvent and without tetramethylsilane as an interior label. Fourier transform infrared spectra (FT–IR) were recorded on a Bruker TENSOR27 infrared spectrophotometer using the KBr pellet technique within the 4000 cm^{-1} to 400 cm^{-1} region. High-resolution mass spectra were obtained using positive mode on Agilent Technologies 6510 Q-TOF LC-MS. The luminescence (excitation and emission) spectra of the samples were determined with a Hitachi F–4500 fluorescence spectrophotometer using a monochromated Xe lamp as an excitation source. Excitation and emission slits measured 5 nm and 2.5 nm, respectively. DSC measurements were studied using SDTQ 600 of TA Instruments. The heating and cooling temperature ramp rates were 10 °C/min. Thermogravimetric analysis (TGA) was performed under N_2 using a TA SDTQ600 at a temperature range of room temperature to 800 °C with a heating rate of 10 °C/min.

Synthesis of D4-1

A cooled oven-dried 25 mL glass vessel was charged with D_4^{Vi} (0.86 g, 2.5 mmol), Ethyl mercaptan (0.62 g, 10 mmol), and DMPA (1 wt%, 0.02 g), and then capped. The vessel was placed under a 100 W UV light (λ_{max} = 365 nm). The reaction mixture was irradiated for 20 min with gentle stirring to yield **D4-1**. After the thiol-ene reaction, the product was purified by precipitation in methanol to eliminate photoinitiator. **D4-1** was obtained as a colorless liquid with a yield of 98%.

Data of **D4-1**:

^{1}H NMR (400 MHz, $CDCl_3$): 0.10-0.25 ($SiC\mathit{H_3}$), 0.86-0.97 ($SiC\mathit{H_2}CH_2$), 1.29-1.37 ($SCH_2C\mathit{H_3}$), 2.61-2.72 ($C\mathit{H_2}SC\mathit{H_2}CH_2Si$). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm): δ = 0.58, ($Si\mathit{C}H_3$), 9.36 ($SCH_2\mathit{C}H_3$), 19.28, ($-Si\mathit{C}H_2CH_2$), 28.13, ($S\mathit{C}H_2CH_2Si$), 30.21, ($S\mathit{C}H_2CH_3$).

D4-2 was obtained as the same way to **D4-1**, yield 93%.

Data of **D4-2**:

^{1}H NMR (400 MHz, $CDCl_3$): 0.13-0.25 ($SiC\mathit{H_3}$), 0.93-1.01 ($SiC\mathit{H_2}CH_2$), 2.59-2.64 ($-C\mathit{H_2}SC\mathit{H_2}-$), 2.79-2.82 ($-SCH_2C\mathit{H_2}COOCH_3$), 3.71 ($-COOC\mathit{H_3}$). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm): δ = 0.03 ($-Si\mathit{C}H_3$), 17.79 ($-Si\mathit{C}H_2CH_2S-$), 26.48 ($-SiCH_2\mathit{C}H_2S-$), 28.83 ($-S\mathit{C}H_2CH_2COOCH_3$), 34.47 ($-\mathit{C}H_2COOCH_3$), 51.68 ($-COO\mathit{C}H_3$), 171.23 ($-\mathit{C}OOCH_3$).

D4-3 was obtained as the same way to **D4-1**, yield 90%.

Data of **D4-3**:

^{1}H NMR (400 MHz, CDCl$_3$): 0.13-0.25 (SiC*H$_3$*), 0.90-0.95 (SiC*H$_2$*CH$_2$), 2.65-2.68 (SiCH$_2$C*H$_2$*SCH$_2$-), 2.70-2.83 (-SCH$_2$C*H*$_2$COOH), 11.64 (-COO*H*). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ = 0.05 (-Si*C*H$_3$), 18.10 (-Si*C*H$_2$CH$_2$S-), 25.45 (-SiCH$_2$*C*H$_2$S-), 26.60 (-S*C*H$_2$CH$_2$COOH), 34.15 (-*C*H$_2$COOH), 172.17 (-*C*OOH).

Data of **T1**:

^{1}H NMR (400 MHz, CDCl$_3$): 0.004 (s, 18H, SiC*H$_3$*), 0.58-0.63 (m, 4H, SiC*H$_2$*CH$_2$), 1.55-1.64 (m, 4H, SiC*H$_2$*C*H$_2$*), 2.55-2.58 (t, 4H, -SiCH$_2$CH$_2$C*H$_2$*SCH$_2$-), 2.72 (s, 4H, -SiCH$_2$CH$_2$CH$_2$SC*H$_2$*-).

Synthesis of POSS-1

In cold glass vessel, OVS (1.0g, 1.58 mmol), Ethyl mercaptan (0.79 g, 12 mmol) and 2 wt% of DMPA were dissolved in 10 ml THF. The mixture was irradiated with stirring for 15 min with UV light at room temperature and then concentrated under reduced pressure. The crude product was washed by CH$_3$OH and the residual solvent was removed under vacuum overnight at room temperature. POSS-1 was obtained as a white powder with a yield of 96%.

Data of **POSS-1**:

^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.06-1.15 (t, -SiC*H$_2$*-, 16H), 1.35-1.39 (t, SCH$_2$C*H$_3$*, 24H), 2.63-2.70 (t, -SiCH$_2$C*H$_2$*-, 16H), 2.71-2.77 (t, -SC*H$_2$*CH$_3$, 16H), ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 12.41 (-Si*C*H$_2$-), 16.80 (SCH$_2$*C*H$_3$), 26.04 (-SiCH$_2$*C*H$_2$S-), 27.09 (-S*C*H$_2$CH$_3$). ^{29}Si NMR (79 Hz, CDCl$_3$, ppm): δ = -68.30.

POSS-2 was obtained as the same way to **D4-1**, yield 93%.

Data of **POSS-2**:

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.01-1.06 (t, -$SiCH_2$-, 16H), 2.60-2.65 (m, -$SiCH_2CH_2SCH_2$-, 32H), 2.79-2.82 (t, -$SCH_2CH_2COOCH_3$, 16H), 3.70 (s, -$COOCH_3$, 16H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.87 (-$SiCH_2$-), 26.04 (-$SiCH_2CH_2S$-), 33.09 (-$SiCH_2CH_2S$-), 52.40 (-SCH_2CH_2CO-), 52.68 (-$COOCH_3$), 172.67 (-$COOCH_3$). ^{29}Si NMR (79 Hz, $CDCl_3$, ppm): δ = -68.54.

Synthesis of P1-ox. (post-oxidation of D4-1)

D4-1 (7.40g, 5.00 mmol) was dissolved in 20 mL THF, set under an argon atmosphere and cooled with an ice bath. Subsequently, 8.00 g oxone (26.0 mmol) was added in and the reaction mixture was stirred for 12 hours slowly warming to room temperature. Another portion of oxone (6.0 mmol) was added and the reaction mixture was stirred for further 12 hours. Afterwards, reaction mixture was filtered, 100 mL trichloromethane was added and the reaction mixture was washed with saturated NaCl solution (3×40 mL). The aqueous phase was again extracted with trichloromethane and the combined organic layers were dried over Na_2SO_4. The solution was concentrated and the product was purified by precipitation in petroleum ether. **P1-ox** was obtained as a viscous liquid with a yield of 55%.

Data of **P1-ox**:

^{1}H NMR (400 MHz, $CDCl_3$): 0.24-0.35 ($SiCH_3$), 1.16-1.20 ($SiCH_2CH_2$), 1.30-1.34 (SCH_2CH_3), 2.79-2.94 ($SO_2CH_2CH_2Si$), 2.94–3.18 ($SO_2CH_2CH_3$). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm): δ = -0.58, ($SiCH_3$), 6.44, (SCH_2CH_3), 25.49, (-$SiCH_2CH_2$), 46.55, ($SO_2CH_2CH_2Si$), 67.80, ($SO_2CH_2CH_3$).

P2-ox was obtained using the same procedure to **P1-ox** as a viscous liquid with a yield of 48%.

Data of **P2-ox**:

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): 0.26 ($\mathrm{SiC}H_3$), 1.14-1.17 ($\mathrm{SiC}H_2\mathrm{CH_2}$), 2.89-2.91 ($\mathrm{-SiCH_2C}H_2\mathrm{SO_2-}$), 3.01-3.06 ($\mathrm{-SO_2C}H_2\mathrm{CH_2COOCH_3}$), 3.34-3.39, ($\mathrm{-SO_2CH_2C}H_2\mathrm{COOCH_3}$), 3.75 ($\mathrm{-COOC}H_3$). ^{13}C NMR (100.62 MHz, $\mathrm{CDCl_3}$, ppm): δ = 0.90 ($\mathrm{-Si}C\mathrm{H_3}$), 25.49 ($\mathrm{-Si}C\mathrm{H_2CH_2SO_2-}$), 26.72 ($\mathrm{-}C\mathrm{H_2COOCH_3}$), 51.68 ($\mathrm{-SiCH_2}C\mathrm{H_2SO_2-}$), 67.79 ($\mathrm{-SO_2}C\mathrm{H_2CH_2COOCH_3}$), 76.94 ($\mathrm{-COO}C\mathrm{H_3}$), 171.03 ($\mathrm{-}C\mathrm{OOCH_3}$).

Data of **P3-ox**:

^{1}H NMR (400 MHz, $\mathrm{CDOD_3}$): 0.26-0.28 ($\mathrm{SiC}H_3$), 1.12-1.29 ($\mathrm{SiC}H_2\mathrm{CH_2}$), 2.79-2.82 ($\mathrm{-SiCH_2C}H_2\mathrm{SO_2-}$), 3.11-3.12 ($\mathrm{-SO_2C}H_2\mathrm{CH_2COOCH_3}$), 3.30-3.41, ($\mathrm{-SO_2CH_2C}H_2\mathrm{COOH}$). ^{13}C NMR (100.62 MHz, $\mathrm{CDOD_3}$, ppm): δ = 0.95 ($\mathrm{-Si}C\mathrm{H_3}$), 24.35 ($\mathrm{-Si}C\mathrm{H_2CH_2SO_2-}$), 31.12 ($\mathrm{-}C\mathrm{H_2COOH}$), 56.38 ($\mathrm{-SiCH_2}C\mathrm{H_2SO_2-}$), 62.51 ($\mathrm{-SO_2}C\mathrm{H_2CH_2COOH}$), 170.18($\mathrm{-}C\mathrm{OOCH}$).

Data of **M1**:

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): 0.04 (s, 18H, $\mathrm{SiC}H_3$), 0.62-0.67 (m, 4H, $\mathrm{SiC}H_2\mathrm{CH_2}$), 1.85-1.93 (m, 4H, $\mathrm{SiC}H_2\mathrm{C}H_2$), 3.09-3.13 (t, 4H, $\mathrm{-SiCH_2CH_2C}H_2\mathrm{SO_2CH_2-}$), 3.44 (s, 4H, $\mathrm{-SiCH_2CH_2CH_2SO_2C}H_2\mathrm{-}$). ^{13}C NMR (100.62 MHz, $\mathrm{CDOD_3}$, ppm): δ = -1.85 ($\mathrm{-Si}C\mathrm{H_3}$), 15.97 ($\mathrm{-Si}C\mathrm{H_2CH_2SO_2-}$), 17.13 ($\mathrm{-SiCH_2}C\mathrm{H_2CH_2SO_2-}$), 44.72 ($\mathrm{-SiCH_2CH_2}C\mathrm{H_2SO_2-}$), 57.73 ($\mathrm{-SiCH_2CH_2CH_2SO_2}C\mathrm{H_2-}$). MS-ESI: 409.1388 $[\mathrm{M + Na}]^{+}$.

POSS-1' was obtained using the same procedure to P1-ox as a white powder with a yield of 50%.

Data of **POSS-1'**:

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.24-1.28 (t, $-SiCH_2-$, 16H), 1.41-1.45 (t, SCH_2CH_3, 24H), 3.05-3.11 (m, $-SiCH_2CH_2SCH_2$, 32H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 14.27 ($-SiCH_2-$), 17.93 ($SO_2CH_2CH_3$), 48.31 ($-SiCH_2CH_2SO_2-$), 50.13 ($-SO_2CH_2CH_3$). ^{29}Si NMR (79 Hz, $CDCl_3$, ppm): δ = -68.80 ppm. MS-ESI: 1406.9970 $[M + Na]^+$, 1385.0198 $[M + H]^+$.

POSS-2' was obtained using the same procedure to P1-ox as a light yellow liquid with a yield of 57%.

Data of **POSS-2'**:

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.25-1.29 (t, $-SiCH_2-$, 16H), 2.86-2.90 (m, $-SiCH_2CH_2SO_2-$, 16H), 3.11-3.15 (m, $-SO_2CH_2CH_2COOCH_3$, 16H), 3.35-3.38 (m, $-SO_2CH_2CH_2COOCH_3$, 16H), 3.73 (s, $-COOCH_3$, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 14.81 ($-SiCH_2-$), 39.01 ($-SiCH_2CH_2SO_2-$), 45.55 ($-SO_2CH_2CH_2CO-$), 49.07 ($-SO_2CH_2CH_2CO-$), 51.87 ($-COOCH_3$), 172.68 ($-COOCH_3$). ^{29}Si NMR (79 Hz, $CDCl_3$, ppm): δ = -68.61. MS-ESI: 1868.0706 $[M + NH_4]^+$.

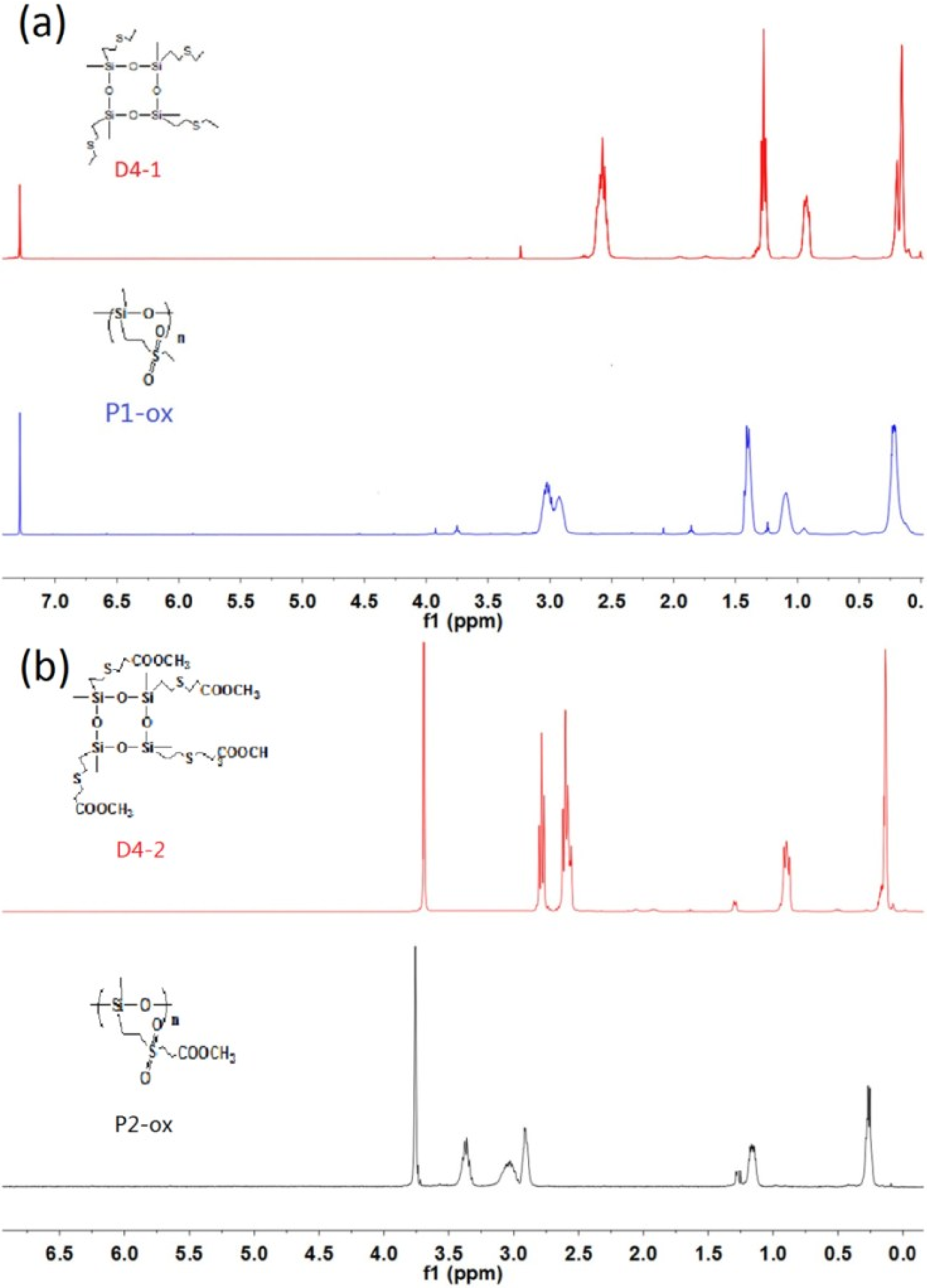


Figure S1. ^{1}H NMR spectra of **D4-1** and **P1-ox** (a) and **D4-2** and **P2-ox** (b).

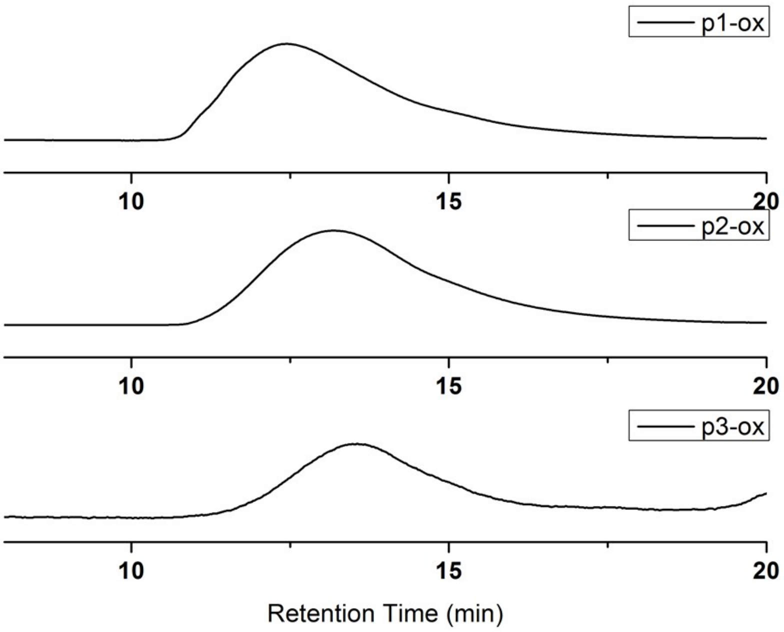


Figure S2. GPC traces of **P1-ox, P2-ox** and **P3-ox.**

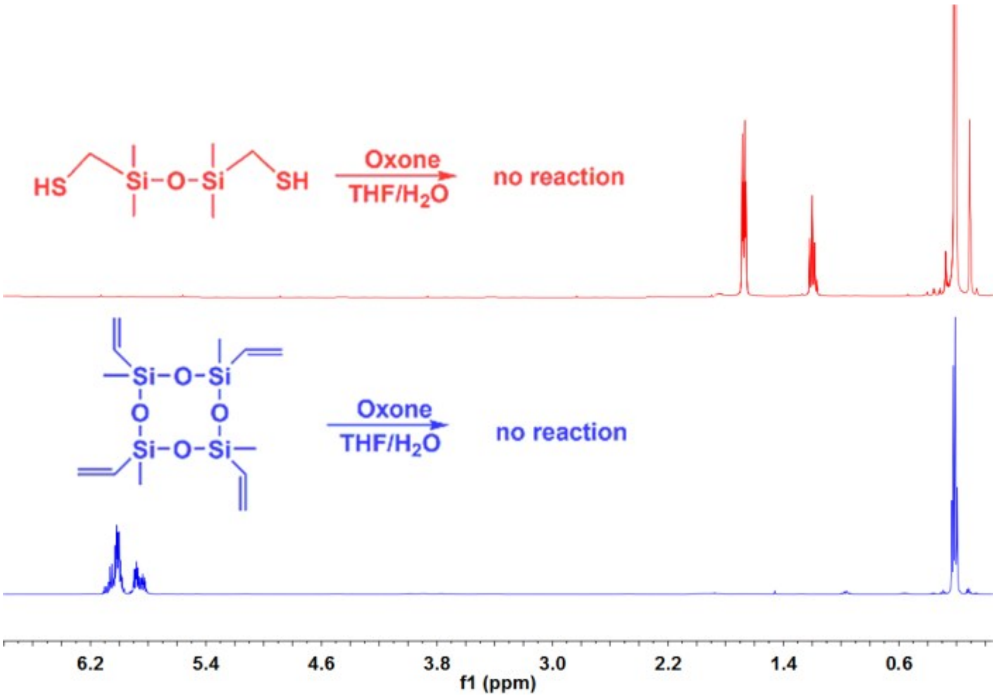
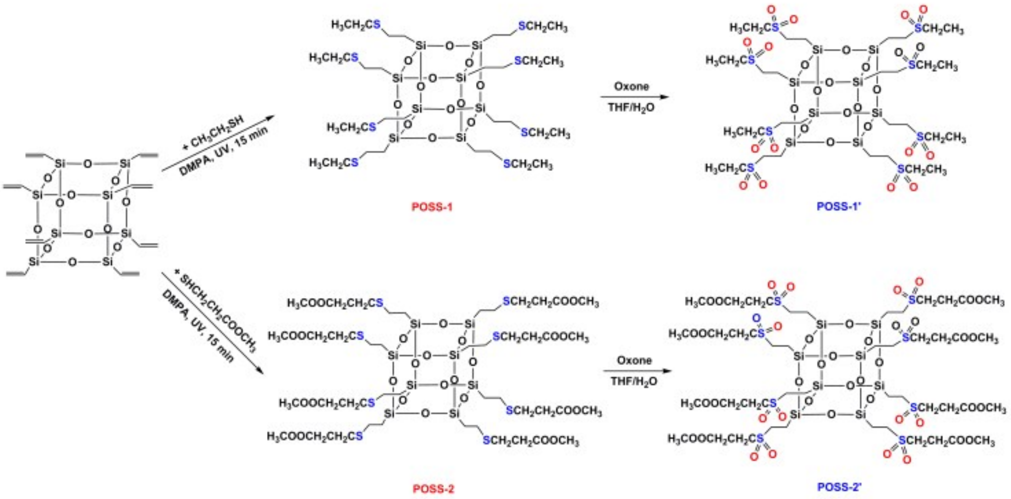


Figure S3. Control experiments of **MM**$^{\mathbf{SH}}$ and **D**$_{\mathbf{4}}^{\mathbf{Vi}}$, and the ^{1}H NMR spectra of the products obtained after oxidation.



Scheme S1. Synthesis routes of **POSS-1**, **POSS-2**, **POSS-1’**, and **POSS-2’**.

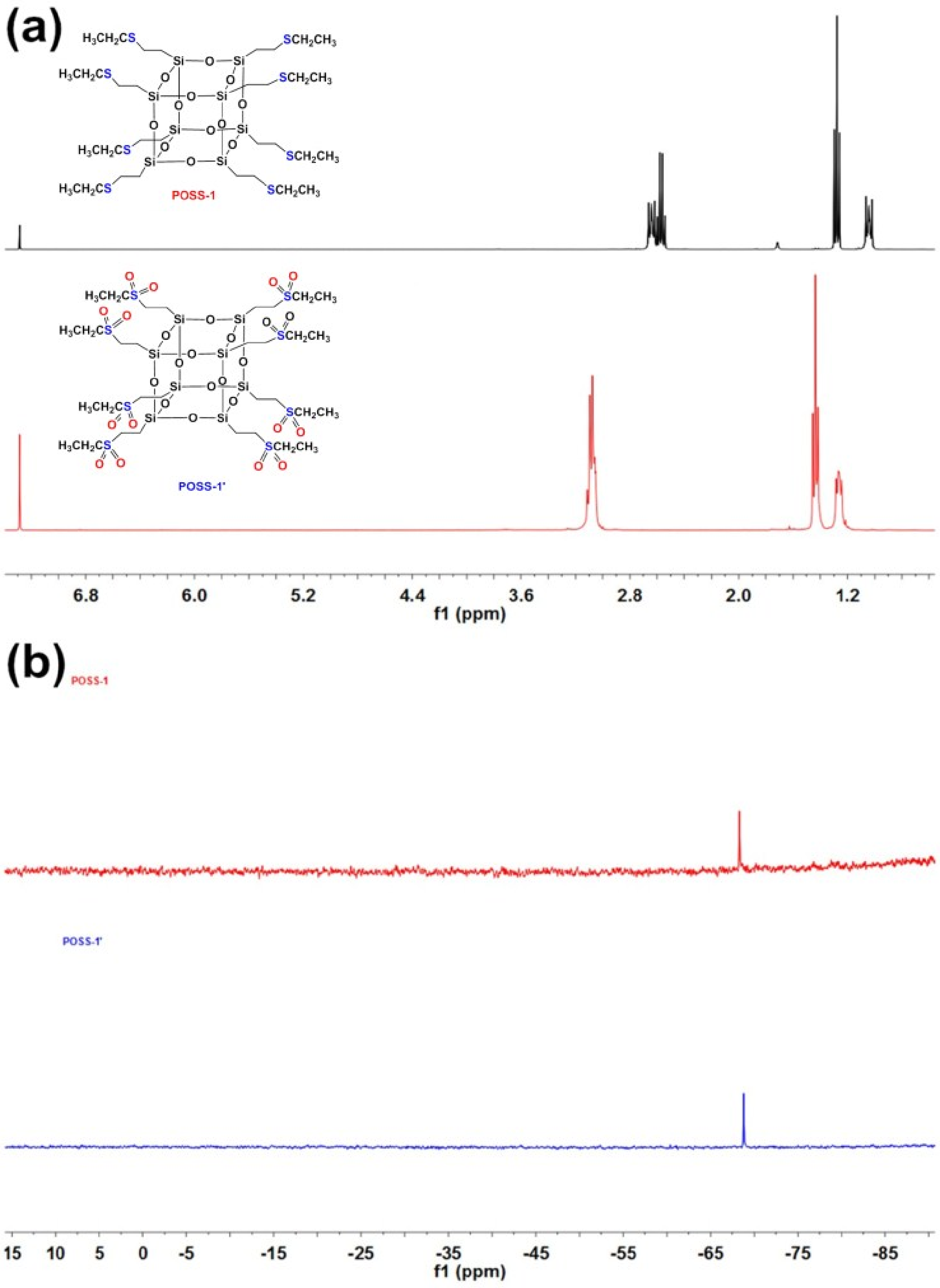


Figure S4. ^1H NMR spectra of **POSS-1** and **POSS-1’** (a) and ^{29}Si NMR spectra of **POSS-1** and **POSS-1’** (b).

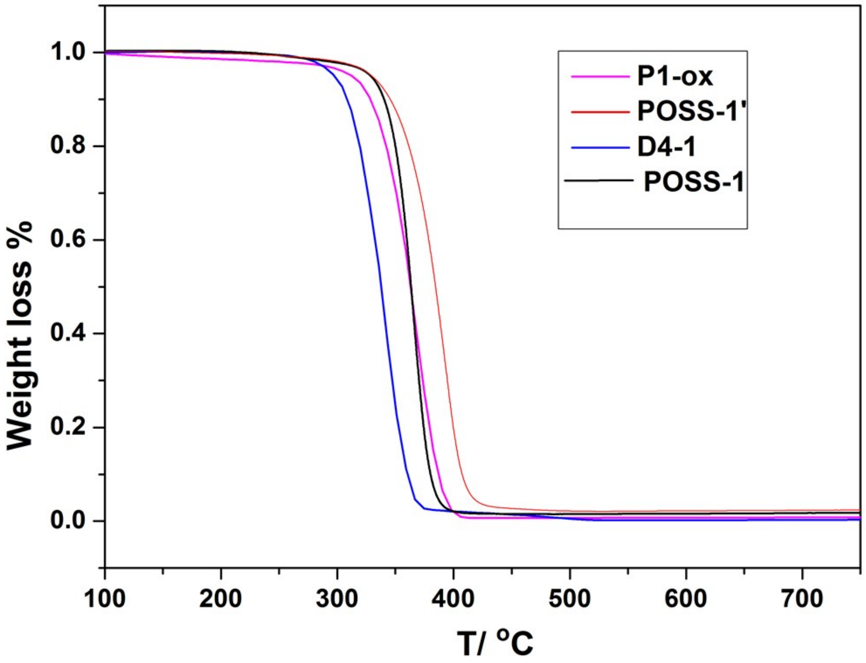


Figure S5. TGA curves of the obtained moleculars.

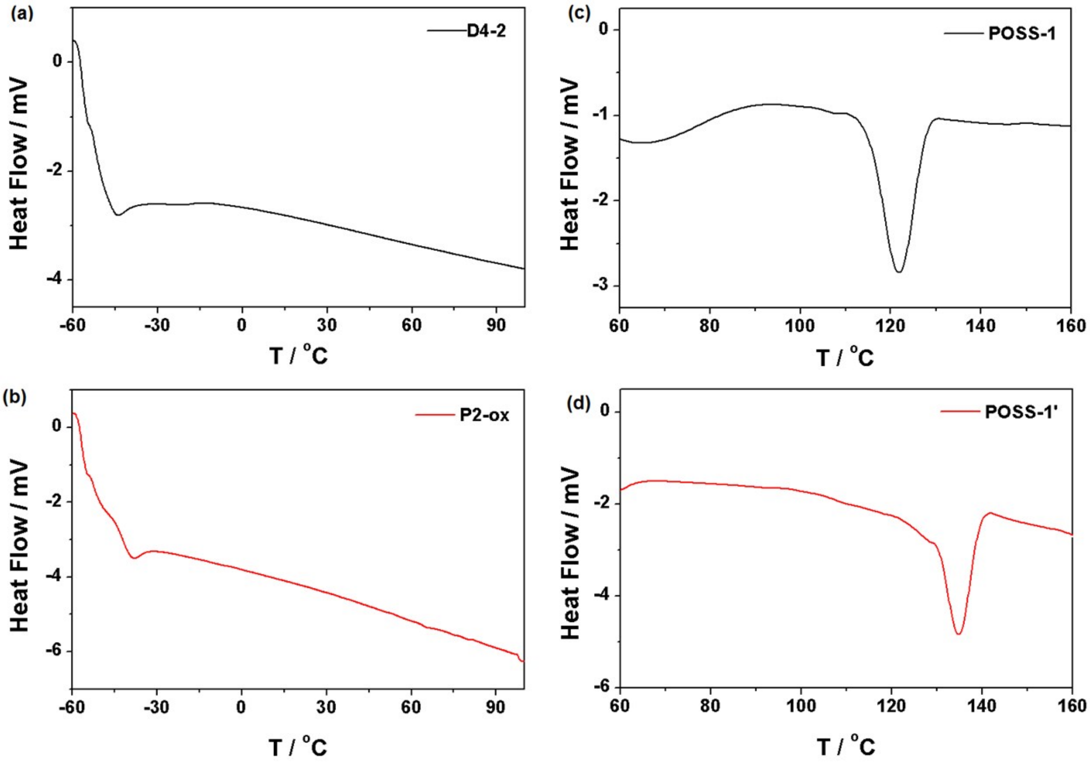


Figure S6. DSC curves of **D4-2** (a), **P2-ox** (b), **POSS-1** (c), and **POSS-1’**(d).