Supporting Information

Effect of strand molecular length on mechanochemical transduction in elastomers probed with uniform force sensors

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Section A. Materials / Instrumentation

1) Materials

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Precursors **a1**, Cl-Si$_4$-H, and **SP-C-500** (**1c**) were prepared according to literature procedures in recent reports.[1–3]

2) Instrumentation

Column chromatography was carried out on silica gel 60F (EMD Millipore, 0.040–0.063 mm) or on aluminum oxide (Sigma-Aldrich, activated, neutral, Brockmann Activity I).

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE III-400 spectrometers, 500 MHz Varian UNITY spectrometer, and Bruker Avance Neo-600 with working frequencies of 400 (^{1}H) and 101 (^{13}C) MHz, 500 MHz (^{1}H) and 126 MHz (^{13}C), and 600 (^{1}H) and 125 (^{13}C) MHz, respectively. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents: $CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm, MeOD: δ_H = 3.31 ppm and δ_C = 49.30 ppm; D_2O: δ_H = 4.79; $(CD_3)_2CO$: δ_H = 2.05 ppm and δ_C = 206.26 ppm. All NMR data in this work were processed using MestReNova.

Size exclusion chromatography (SEC) analyses were carried out on an Agilent 1260 Infinity system with dual Agilent PL1110-6500 columns using a chloroform mobile phase at a flow rate of 1 mL/min.

High resolution mass spectrometry (HRMS) was performed on a high-resolution JEOL AccuTOF 4G LC-plus equipped with an ionSense DART (Direct Analysis in Real Time) source using as a calibration standard in MIT or with an Agilent LCMS-TOF-DART at Mass Spectrometry Facility in Duke University.

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra were measured on a high-resolution Bruker Autoflex LRF Speed mass spectrometer using dithranol as the matrix and chloroform as the solvent.

The small-angle X-ray scattering (SAXS), middle-angle X-ray scattering (MAXS), and wide-angle X-ray scattering (WAXS) for the PDMS films were performed with SAXSLab Ganesha using Cu 50kV Xenocs Genix ULD SL X-ray Source.

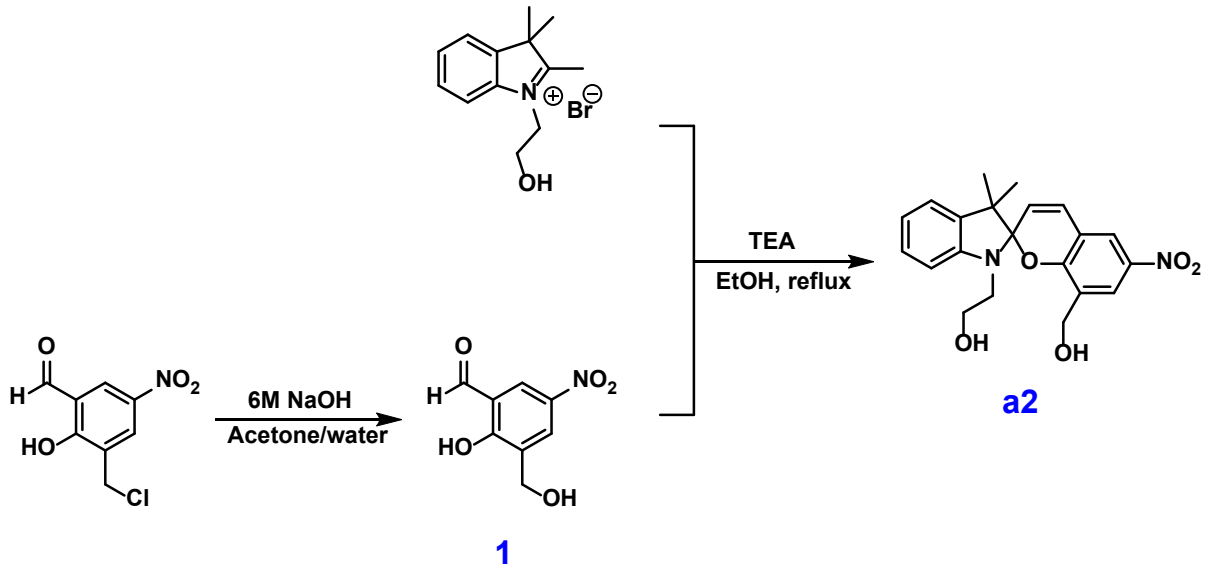
Tensile test was performed by Dynamic Mechanical Analyzer (DMA) TA Instruments RSA III at Shared Materials Instrumentation Facility (SMiF) in Duke University. During the tensile test, the

images were taken with a Canon EOS RebelTM xsi with a Cannon EF-S 18-55 mm f/3.5-5.6 IS SLR lens.

UV-vis measurements were performed with Photonics Model 440 UV-Vis Spectrophotometer.

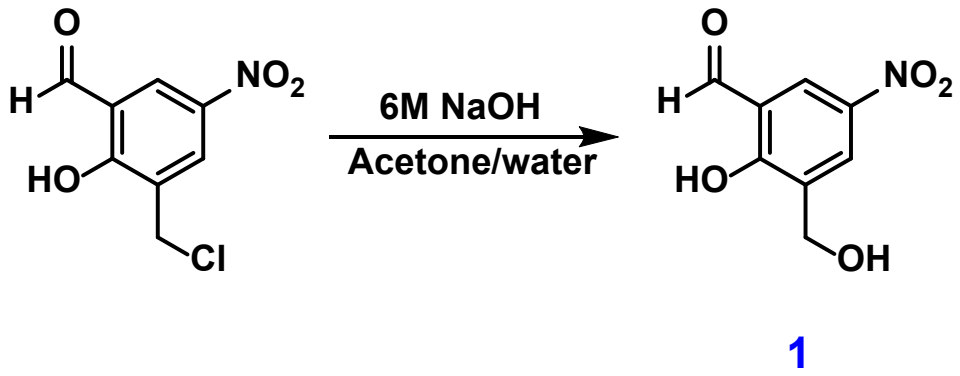
Section B. Synthetic Protocols

1) Synthesis of spiropyran (SP) derivatives



Scheme S1 General synthesis scheme of SP derivatives

Synthesis of 1

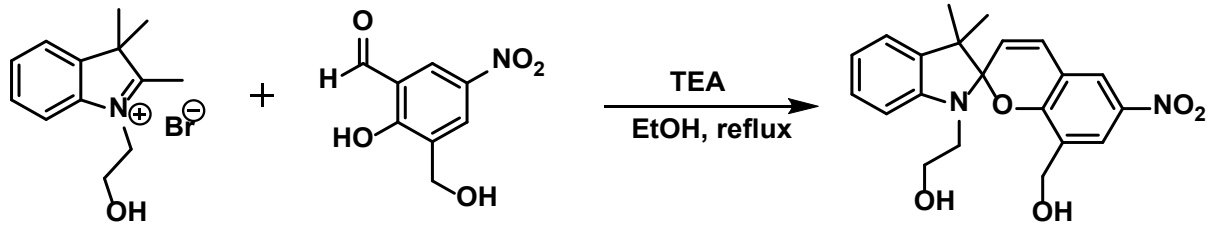


Scheme S2 Synthesis of **1**.

The molecule **1** was synthesized with the similar procedure as previous study.[4]

1: To the flask, 3-chloromethyl-5-nitrosalicylaldehyde (8 g, 37.1 mmol) was added, followed by dissolving in acetone (41.80 ml) and DI water (13.93 ml) mixture. The reaction mixture was heated at 65 °C for 20 min to reflux, then 6 M of sodium hydroxide solution (6.2 ml) was slowly added from an addition funnel. After 3 h, the reaction mixture was cooled to the room temperature and filtered. The filtrate was stored in a fridge to precipitate chemicals. After filtration, the chemicals were further purified by recrystallization from DI water, and green crystals were obtained as products (4.8 g, 65.8% yield). HRMS-ESI: Calcd for $C_8H_7NO_5$: *m/z* = 198.0397 $[M + H]^+$, 220.0216 $[M+Na]^+$; Found: 198.0399 $[M +H]^+$, 220.0223 $[M+Na]^+$. ^1H NMR (500 MHz, $(CD_3)_2CO$, ppm): δ_H 11.92 (b, 1H), 10.20 (s, 1H), 8.68 (d, J = 1.4 Hz, 1H), 8.58 (m, 1H), 4.79 (s, 2H), 4.71 (b, 1H). ^{13}C NMR (126 MHz, $(CD_3)_2CO$, ppm): δ_C 198.26, 163.50, 141.57, 133.86, 129.01, 128.71, 120.29, 58.30.

Synthesis of a2



1 **a2**

Scheme S3 Synthesis of **a2** from **1**.

The molecule **a2** was synthesized by the similar procedure in the previous study.[1]

2a: 2-hydroxyethyl-2,3,3-trimethyl-3H-indolium bromide (3.6 g, 12.68 mmol) and **1** (2.5 g, 12.68 mmol) was added to a flask and dissolved in ethanol (105 ml). To the mixture, 3.54 ml of triethylamine (25.36 mmol) was subsequently added. Then, the reaction mixture was heated to 100 °C to reflux for 5 h, followed by cooling to the room temperature. The mixture was concentrated under reduced pressure and dissolved in dichloromethane. Then, the solution was washed with DI water (3x) and Brine (1x), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure, and the product was further dried under high vacuum (3.90 g, 80.5% yield). HRMS-ESI: Calcd for $C_{21}H_{22}N_2O_5$: *m/z* = 383.1602 $[M + H]^+$; Found: 383.1607 [*M*

+H]$^+$. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, ppm): δ_H 8.23 (d, J = 2.7 Hz, 1H), 8.04 (d, J = 2.9 Hz, 1H), 7.16 (d, J = 10.4 Hz, 1H), 7.13 – 7.11 (m, 2H), 6.83 – 6.80 (m, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.06 (d, J = 10.4 Hz, 1H), 4.45 – 4.41 (m, 2H), 3.75 – 3.70 (m, 1H), 3.66 – 3.61 (m, 1H), 3.43 – 3.37 (m, 1H), 3.31 – 3.25 (m, 1H), 1.28 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (126 MHz, $(CD_3)_2CO$, ppm): δ_C 156.51, 148.14, 141.86, 136.77, 130.67, 129.00, 128.45, 123.42, 122.93, 122.43, 121.86, 120.17, 119.32, 107.78, 107.59, 60.75, 58.43, 53.25, 46.91, 26.22, 20.22.

2) Synthesis of discrete spiropyran-incorporated crosslinkers

Discrete SP force probes

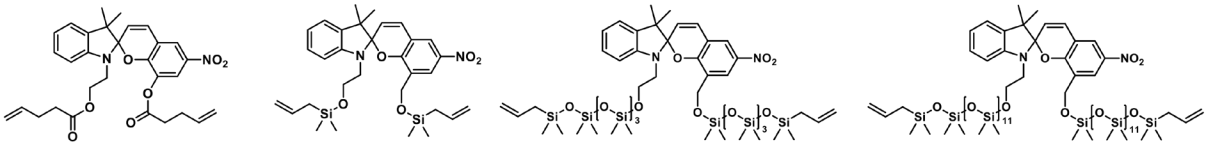
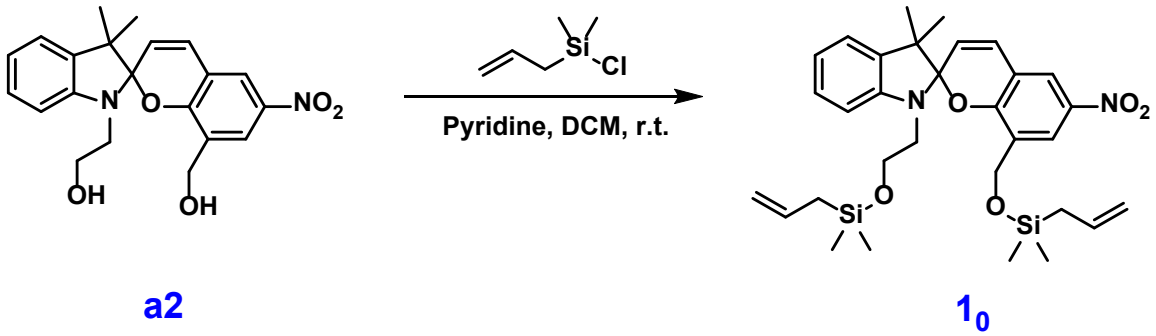


Fig. S1 Discrete SP force probes used in this study.

The synthesis of SP-C-500 ($\mathbf{1_c}$) was reported in the previous study.[1]

Synthesis of SP-PDMS-500 ($\mathbf{1_0}$)

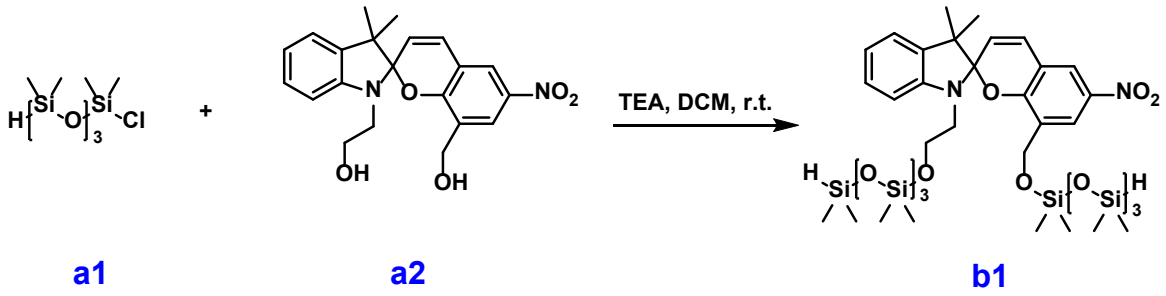


Scheme S4 Synthesis of $\mathbf{1_0}$ from **a2**.

1_0: Allyl(chloro)dimethylsilane (116.3 mg, 130.5 µL, 0.86 mmol) was first dissolved in DCM (1 mL). Pyridine (82.5 mg, 84.0 µL, 1.04 mmol) was then dissolved in dichloromethane (DCM) (1 mL) and then added dropwise into the solution of Allyl(chloro)dimethylsilane under ice bath. The

reaction solution was left stirring for 10 minutes before dropwise adding the solution of spiropyran (110.0 mg, 0.29 mmol) to the reaction solution. After completion of the addition, ice bath was removed and the reaction solution was left overnight at room temperature. After the completion of the reaction, 100 mL of DCM was added to the mixture. The organic solution was extracted 2x with 150 mL of H_2O and 1x with 150 mL of brine solution. The organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (Hexanes/EtOAc) to afford the final product $\mathbf{1_0}$ as a dark purple liquid (142.1 g, 0.24 mmol, 85% yield). HRMS-ESI: Calcd for $C_{31}H_{42}N_2O_5Si_2$: *m/z* = 578.26 $[M + H]^+$; Found: 579.27050 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 8.19 (d, J = 2.8 Hz, 1H), 7.94 (d, J = 2.8 Hz, 1H), 7.19 (td, J = 7.7, 1.3 Hz, 1H), 7.09 (dd, J = 7.3, 1.3 Hz, 1H), 6.96 – 6.83 (m, 2H), 6.62 (d, J = 7.7 Hz, 1H), 5.88 (d, J = 10.4 Hz, 1H), 5.84 – 5.64 (m, 2H), 4.94 – 4.73 (m, 4H), 4.53 – 4.35 (m, 2H), 3.83 – 3.61 (m, 2H), 3.47 – 3.16 (m, 2H), 1.62 – 1.52 (m, 4H), 1.27 (s, 3H), 1.19 (s, 3H), 0.09 (s, 6H), 0.06 (d, J = 1.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ_C 155.62, 146.91, 140.95, 135.62, 134.38, 128.48, 128.18, 128.08, 127.81, 127.65, 124.12, 123.56, 121.89, 121.84, 121.70, 121.60, 121.25, 119.75, 119.58, 117.88, 113.31, 106.88, 106.78, 106.61, 77.34, 77.22, 77.02, 76.70, 60.19, 60.06, 58.09, 52.66, 52.55, 45.77, 26.27, 25.88, 19.88, 1.42, 1.14, 1.05, 1.00, 0.97, 0.83, 0.68, 0.32, -0.29, -1.15, -1.25.

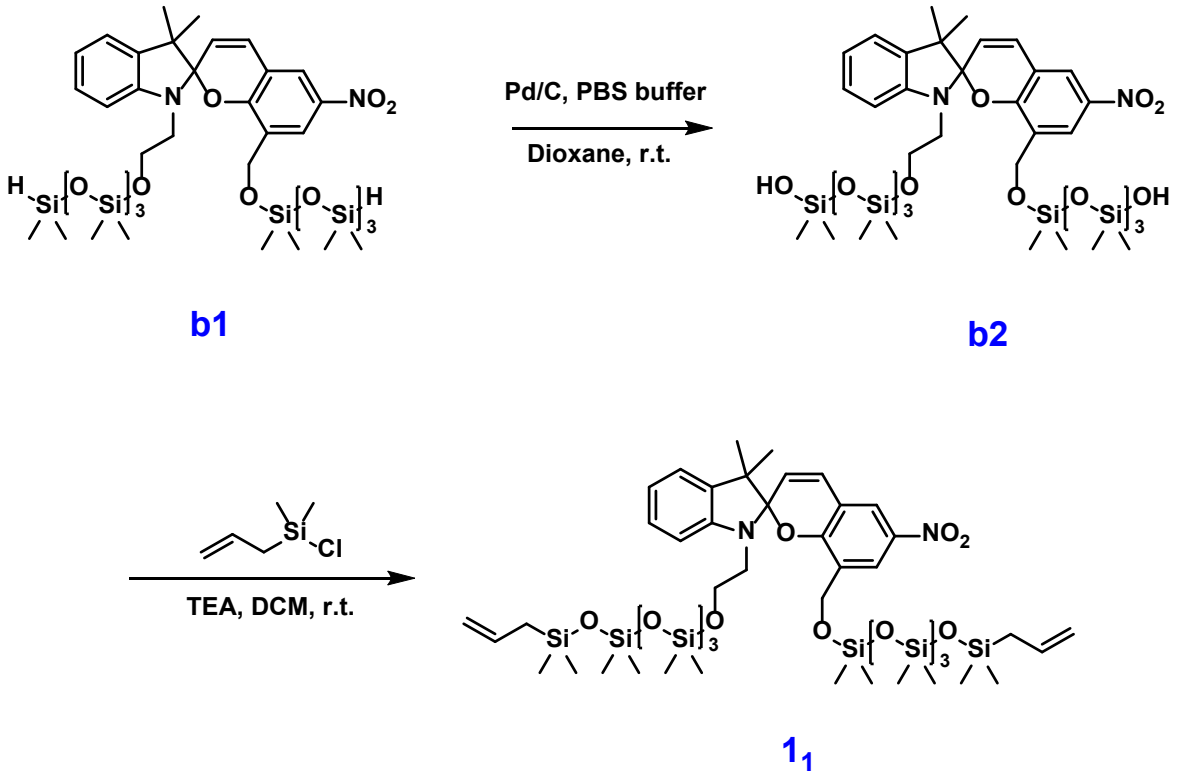
*Synthesis of SP-PDMS-1k (**1$_1$**)*



Scheme S5 Synthesis of **b1** from **a1** and **a2**.

b1: a1 (2.6 g, 7.86 mmol) was dissolved in DCM (10 mL) under ice bath. Triethyl amine (TEA) (926.9 mg, 1.27 mL, 9.16 mmol) was then dissolved in 5 mL DCM and then added dropwise into the solution of **a1**. The reaction solution was left stirring for 10 minutes before dropwise adding

a2 (1.0 g, 2.62 mmol) to the reaction solution. After completion of the addition, ice bath was removed and the reaction solution was left overnight at room temperature. After the completion of the reaction, 300 mL of DCM was added to the mixture. The organic solution was extracted 2x with 450 mL of H_2O and 1x with 400 mL of brine solution. The organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (Hexanes/EtOAc) to afford the final product **b1** as a dark purple liquid (1.72 g, 1.83 mmol, 70% yield). HRMS-ESI: Calcd for $C_{37}H_{70}N_2O_{11}Si_8$: *m/z* = 942.31 $[M + H]^+$; Found: 943.32065 $[M +H]^+$. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ_H 8.23 (d, J = 2.8 Hz, 1H), 7.93 (d, J = 2.7 Hz, 1H), 7.16 (td, J = 7.6, 1.3 Hz, 1H), 7.06 (dd, J = 7.3, 1.2 Hz, 1H), 6.95 – 6.79 (m, 2H), 6.62 (d, J = 7.7 Hz, 1H), 5.88 (d, J = 10.4 Hz, 1H), 4.71 (tq, J = 5.6, 2.8 Hz, 2H), 4.50 (q, J = 14.5 Hz, 2H), 3.90 – 3.68 (m, 2H), 3.50 – 3.18 (m, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 0.28 – 0.17 (m, 12H), 0.11 – 0.06 (m, 24H), 0.03 (s, 6H), -0.03 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ_C 155.63, 146.91, 140.94, 135.62, 128.48, 128.08, 127.67, 123.57, 121.90, 121.62, 121.26, 119.58, 117.89, 106.89, 106.62, 77.24, 77.03, 76.82, 60.20, 58.11, 52.57, 45.77, 25.91, 19.91, 0.99, 0.96, 0.86, 0.83, 0.81, 0.69, 0.58, -1.13, -1.15, -1.22, -1.26.



b1 **b2** $\mathbf{1_1}$

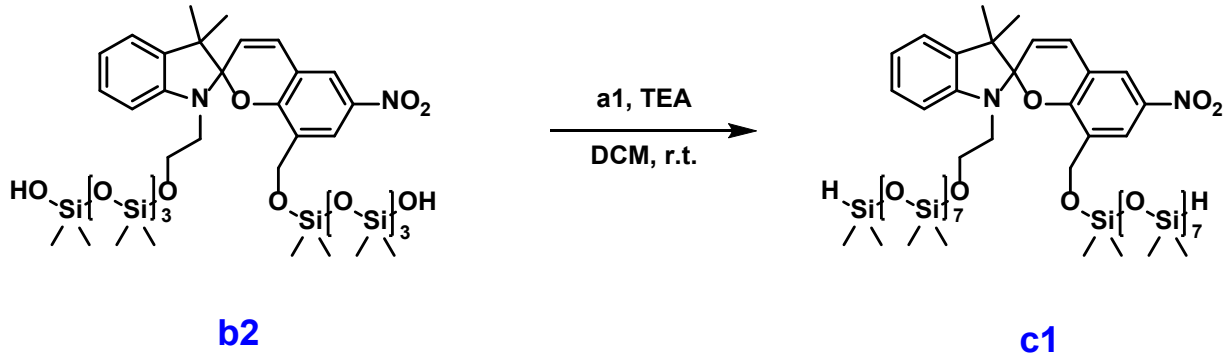
Scheme S6 Synthesis of $\mathbf{1_1}$ from **b1**.

1_1: b1 (1.0 g, 1.06 mmol) was firstly dissolved in dioxane (10 mL) and was put under ice bath. Pd/C (22.6 mg, 21.2 μmol) was suspended in PBS buffer (5 mL) and then added dropwise into the solution of **b1**. The reaction solution was left stirring in ice bath for 30 minutes. Then, the ice bath was removed and the reaction system was left to further react for another 2 hours at room temperature utill completion. After completion of the addition, the reaction solution was firstly filtered through a filter paper to remove Pd/C and rinsed with a total of 200 mL of DCM. The organic solution was combined and then extracted 2x with 250 mL of H_2O and 1x with 250 mL of brine solution. After three rounds of extraction, the organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum with around 2 mL of DCM left. The crude product **b2** in DCM was used directly for the next steps.

Allyl(chloro)dimethylsilane (94.3 mg, 105.8 μL, 0.70 mmol) was first dissolved in DCM (1 mL). TEA (79.9 mg, 110.1 μL, 0.79 mmol) was then dissolved in dichloromethane (DCM) (1 mL) and then added dropwise into the solution of Allyl(chloro)dimethylsilane under ice bath. The reaction solution was left stirring for 10 minutes before dropwise adding the solution of **b2** (165.6 mg, 0.17 mmol) to the reaction solution. After completion of the addition, ice bath was removed and the

reaction solution was left overnight at room temperature. After the completion of the reaction, 100 mL of DCM was added to the mixture. The organic solution was extracted 2x with 150 mL of H_2O and 1x with 150 mL of brine solution. The organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (Hexanes/EtOAc) to afford the final product $\mathbf{1_1}$ as a dark purple liquid (152.1 mg, 0.13 mmol, 79% yield). HRMS-ESI: Calcd for $C_{47}H_{90}N_2O_{13}Si_{10}$: *m/z* = 1170.41 $[M + H]^+$; Found: 1171.42083 $[M+H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 8.22 (d, J = 2.7 Hz, 1H), 7.93 (d, J = 2.8 Hz, 1H), 7.16 (td, J = 7.7, 1.3 Hz, 1H), 7.06 (dd, J = 7.3, 1.3 Hz, 1H), 6.97 – 6.79 (m, 2H), 6.62 (d, J = 7.7 Hz, 1H), 5.97 – 5.71 (m, 3H), 4.97 – 4.79 (m, 4H), 4.50 (q, J = 14.5 Hz, 2H), 3.89 – 3.61 (m, 2H), 3.51 – 3.16 (m, 2H), 1.60 (s, 2H), 1.57 (s, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 0.13 – 0.03 (m, 54H), -0.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ_C 155.62, 146.91, 140.95, 135.62, 134.31, 128.47, 128.08, 127.65, 123.57, 121.90, 121.61, 121.26, 119.58, 113.38, 106.89, 106.61, 77.34, 77.02, 76.70, 60.20, 58.09, 52.56, 45.77, 26.26, 25.89, 19.89, 1.14, 1.07, 1.02, 0.99, 0.85, -0.28, -1.14, -1.24.

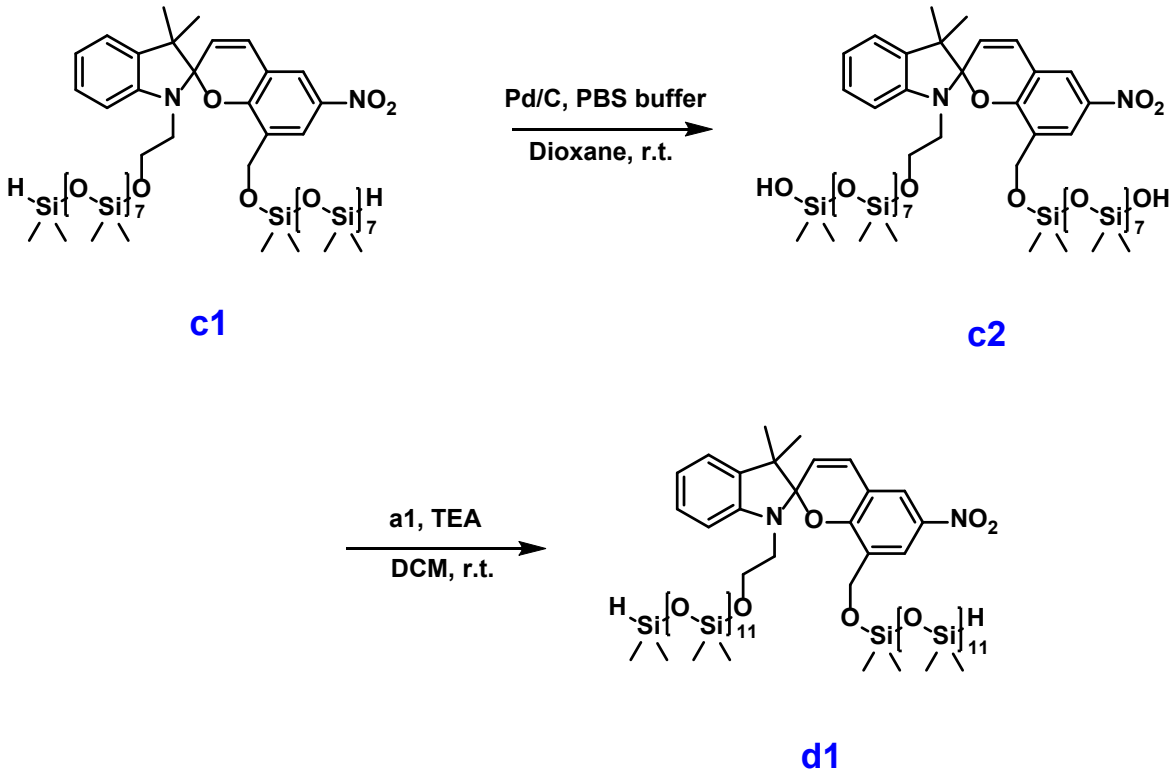
*Synthesis of SP-PDMS-2k (**1_3**)*



Scheme S7 Synthesis of **c1** from **b2**.

c1: In a solution of **a1** (0.86 g, 2.71 mmol) in DCM (5 mL), TEA (308.6 mg, 425.1 µL, 3.05 mmol) was added dropwise under ice bath and was left stirring for 10 minutes. The solution of **b2** (0.66 g, 0.68 mmol) in DCM was then added dropwise into the reaction solution. After completion of the addition, ice bath was removed and the reaction solution was left overnight at room temperature. After the completion of the reaction, 200 mL of DCM was added to the mixture. The organic solution was extracted 2x with 250 mL of H_2O and 1x with 250 mL of brine solution. The organic

layer was isolated, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (Hexanes/EtOAc) to afford the final product **c1** as a dark purple liquid (0.81 g, 0.53 mmol, 78% yield). HRMS-ESI: Calcd for $C_{53}H_{118}N_2O_{19}Si_{16}$: *m/z* = 1534.46 $[M + H]^+$; Found: 1536.47881 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 8.22 (d, J = 2.7 Hz, 1H), 7.93 (d, J = 2.8 Hz, 1H), 7.16 (td, J = 7.7, 1.3 Hz, 1H), 7.06 (dd, J = 7.3, 1.4 Hz, 1H), 6.97 – 6.79 (m, 2H), 6.62 (d, J = 7.8 Hz, 1H), 5.88 (d, J = 10.4 Hz, 1H), 4.73 (h, J = 3.0 Hz, 2H), 4.59 – 4.41 (m, 2H), 3.80 (t, J = 7.1 Hz, 2H), 3.49 – 3.19 (m, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 0.21 (d, J = 2.8 Hz, 12H), 0.14 – 0.05 (m, 78H), -0.02 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ_C 155.63, 146.91, 140.94, 135.62, 128.48, 128.08, 127.81, 127.65, 124.11, 123.57, 121.90, 121.84, 121.61, 121.26, 119.58, 117.89, 106.89, 106.61, 77.24, 77.02, 76.81, 60.19, 58.09, 52.56, 45.77, 25.89, 19.89, 1.30, 1.06, 1.04, 1.01, 0.98, 0.87, 0.84, 0.81, 0.70, 0.33, -1.15, -1.24.

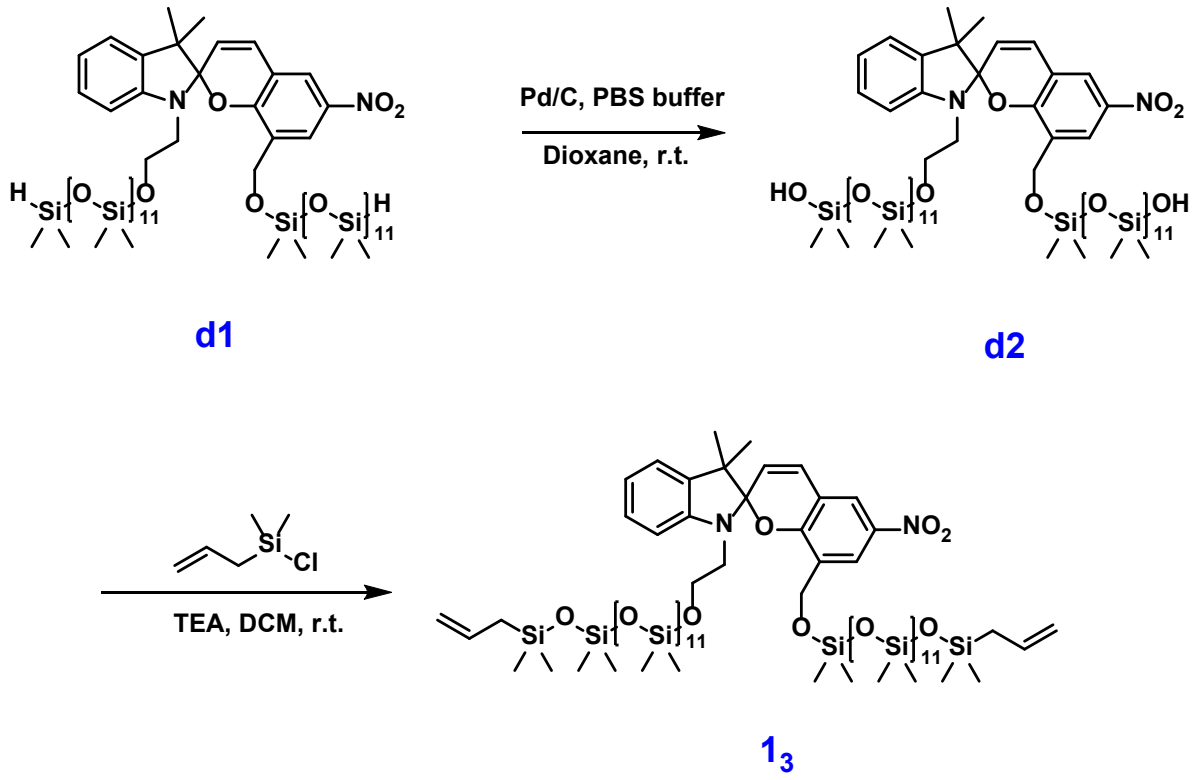


Scheme S8 Synthesis of **d1** from **c1**.

d1: **c1** (322.4 mg, 0.21 mmol) was firstly dissolved in dioxane (1 mL) and was put under ice bath. Pd/C (4.6 mg, 4.2 μmol) was suspended in PBS buffer (0.5 mL) and then added dropwise

into the solution of **c1**. The reaction solution was left stirring in ice bath for 30 minutes. Then, the ice bath was removed and the reaction system was left to further react for another 2 hours at room temperature utill completion. After completion of the addition, the reaction solution was firstly filtered through a filter paper to remove Pd/C and rinsed with a total of 100 mL of DCM. The organic solution was combined and then extracted 2x with 150 mL of H_2O and 1x with 150 mL of brine solution. After three rounds of extraction, the organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum with around 2 mL of DCM left. The crude product **c2** in DCM was used directly for the next steps.

In a solution of **a1** (266.0 mg, 298.6 µL, 0.84 mmol) in DCM (1 mL), TEA (96.1 mg, 132.4 µL, 0.95 mmol) was added dropwise under ice bath and was left stirring for 10 minutes. The solution of **c2** in DCM was then added dropwise into the reaction solution. After completion of the addition, ice bath was removed and the reaction solution was left overnight at room temperature. After the completion of the reaction, 200 mL of DCM was added to the mixture. The organic solution was extracted 2x with 250 mL of H_2O and 1x with 250 mL of brine solution. The organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by preparative gel permeation chromatography (GPC) in Chloroform to afford the final product **d1** as a dark purple liquid (382.9 mg, 0.18 mmol, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 8.22 (d, J = 2.7 Hz, 1H), 7.93 (d, J = 2.8 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 6.94 – 6.80 (m, 2H), 6.62 (d, J = 7.8 Hz, 1H), 5.88 (d, J = 10.4 Hz, 1H), 4.73 (p, J = 2.8 Hz, 2H), 4.49 (q, J = 14.6 Hz, 2H), 3.89 – 3.68 (m, 2H), 3.39 (q, J = 7.3 Hz, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 0.21 (d, J = 2.8 Hz, 12H), 0.13 – 0.05 (m, 126H), -0.02 (d, J = 1.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ_C 155.60, 146.85, 140.96, 135.62, 128.31, 128.14, 127.69, 123.61, 121.83, 121.65, 121.33, 119.63, 117.91, 106.88, 106.66, 77.34, 77.22, 77.02, 76.70, 60.29, 58.16, 52.56, 45.64, 25.90, 19.92, 0.98, 0.96, 0.84, 0.34, 0.32, -1.18, -1.20, -1.24, -1.30.



Scheme S9 Synthesis of **1₃** from **d1**.

1₃: d1 (259.1 mg, 0.12 mmol) was firstly dissolved in dioxane (1 mL) and was put under ice bath. Pd/C was suspended in PBS buffer (0.5 mL) and then added dropwise into the solution of **d1**. The reaction solution was left stirring in ice bath for 30 minutes. Then, the ice bath was removed and the reaction system was left to further react for another 2 hours at room temperature utill completion. After completion of the addition, the reaction solution was firstly filtered through a filter paper to remove Pd/C (2.6 mg, 2.4 μmol) and rinsed with a total of 100 mL of DCM. The organic solution was combined and then extracted 2x with 150 mL of H_2O and 1x with 150 mL of brine solution. After three rounds of extraction, the organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum with around 1 mL of DCM left. The crude product **d2** in DCM was used directly for the next steps.

Allyl(chloro)dimethylsilane (64.6 mg, 72.5 μL, 0.48 mmol) was first dissolved in DCM (1 mL). TEA (54.6 mg, 75.9 μL, 0.54 mmol) was then dissolved in dichloromethane (DCM) (1 mL) and then added dropwise into the solution of Allyl(chloro)dimethylsilane under ice bath. The reaction solution was left stirring for 10 minutes before dropwise adding the solution of **d2** to the reaction solution. After completion of the addition, ice bath was removed, and the reaction solution was

left overnight at room temperature. After the completion of the reaction, 100 mL of DCM was added to the mixture. The organic solution was extracted 2x with 150 mL of H_2O and 1x with 150 mL of brine solution. The organic layer was isolated, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by preparative GPC in Chloroform to afford the final product **1₃** as a dark purple liquid (220.2 mg, 0.09 mmol, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 1H NMR (400 MHz, CDCl3) δ 8.22 (d, J = 2.7 Hz, 1H), 7.93 (d, J = 2.8 Hz, 1H), 7.23 – 7.10 (m, 1H), 7.09 – 7.03 (m, 1H), 6.95 – 6.79 (m, 2H), 6.62 (d, J = 7.7 Hz, 1H), 5.95 – 5.69 (m, 3H), 4.99 – 4.77 (m, 4H), 4.49 (d, J = 13.2 Hz, 2H), 3.88 – 3.66 (m, 2H), 3.39 (d, J = 7.3 Hz, 2H), 1.68 – 1.44 (m, 4H), 1.27 (s, 3H), 1.19 (s, 3H), 0.13 – 0.05 (m, 156H), 0.04 (s, 6H), -0.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 155.62, 146.91, 140.95, 135.62, 134.38, 128.48, 128.08, 127.65, 123.56, 121.89, 121.60, 121.25, 119.58, 117.88, 113.31, 106.88, 106.61, 77.34, 77.22, 77.02, 76.70, 67.11, 60.19, 58.09, 52.55, 45.77, 26.27, 25.88, 19.89, 1.42, 1.14, 1.05, 1.00, 0.97, 0.83, 0.69, -0.29, -1.15, -1.25.

3) Synthesis of PDMS elastomer with SP force probes

For general PDMS with SP probe samples, 1.01×10^{-2} mmol of SP molecule was dissolved in 0.12 ml of xylene: 5.86 mg for SP-PDMS-500 (**1₀**), 11.86 mg for SP-PDMS-1k (**1₁**), 23.83 mg for SP-PDMS-2k (**1₃**), and 5.38 mg for SP-C-500 (**1c**). Then, PDMS Sylgard 184 base (1 g) and curing agent (0.1 g) was poured into the solution (Base:curing agent = 10:1), followed by mixing with vortex. After becoming homogeneous, the solution was centrifuged just ~10 s at 4500 rpm to remove visible bubbles and poured into a PTFE mold. After leaving on a flat surface for 1 h at room temperature, the sample was cured at 58 °C in an oven for 16.5 h. For the samples with other base:curing agent ratios, the same procedure with the following recipes was used; For 10:1 (Base : curing agent) sample, SP-C-500 (**1c**) (5.38 mg, 1.01×10^{-2} mmol), base (1 g), curing agent (0.1 g), xylene (120 ml); For 8:1 sample: SP-C-500 (**1c**) (5.51 mg, 1.03×10^{-2} mmol), base (1 g), curing agent (0.125 g), xylene (123 ml); For 12:1 sample: SP-C-500 (**1c**) (5.31 mg, 1.00×10^{-2} mmol), base (1 g), curing agent (0.83 g), xylene (118 ml).

Table S1 Fabricated PDMS elastomers with SP probes

Sample ID	Batch #	*M*n of force probe (g/mol)	Base:curing agent	Modulus (MPa)	*M*x[a)] (g/mol)	ε_{SH}[b)]
PDMS/SP-PDMS-500 (**1**$_0$)	1	578	10:1	1.14	3080	0.83
	2			0.98	3570	0.93
PDMS/SP-PDMS-1k (**1**$_1$)	1	1170		1.16	3040	0.85
	2			1.07	3290	0.88
PDMS/SP-PDMS-2k (**1**$_3$)	1	2356		1.08	3250	0.89
	2			1.11	3170	0.86
PDMS/SP-C-500 (**1c**) (8:1)	1	533	8:1	0.94	3730	0.78
PDMS/SP-C-500 (**1c**) (12:1)	1		12:1	0.62	5670	1.32
PDMS/SP-C-500 (**1c**) (10:1)	1		10:1	0.76	4630	1.03
	2			0.84	4170	0.98
	3			0.98	3600	0.93

a) *M*x is the molecular weight between crosslinkers and calculated as *M*x = $\frac{3\rho RT(f-2)}{Ef}$, where ρ, R, T, E, and f are density, gas constant, temperature, Young Modulus, and functionality (f = 4), respectively; [b)] ε_{SH} the critical strain based on stress-strain curves

Section C. X-ray Scattering of the PDMS-SP films

The small-angle X-ray scattering (SAXS), middle-angle X-ray scattering (MAXS), and wide-angle X-ray scattering (WAXS) for the PDMS films were conducted with SAXSLab Ganesha equipped with Cu 50kV Xenocs Genix ULD SL X-ray Source. For all scattering vector regimes, there is no obvious difference between the PDMS with SP samples and one without SP, indicating no or little (if any) aggregation of the SP probes.

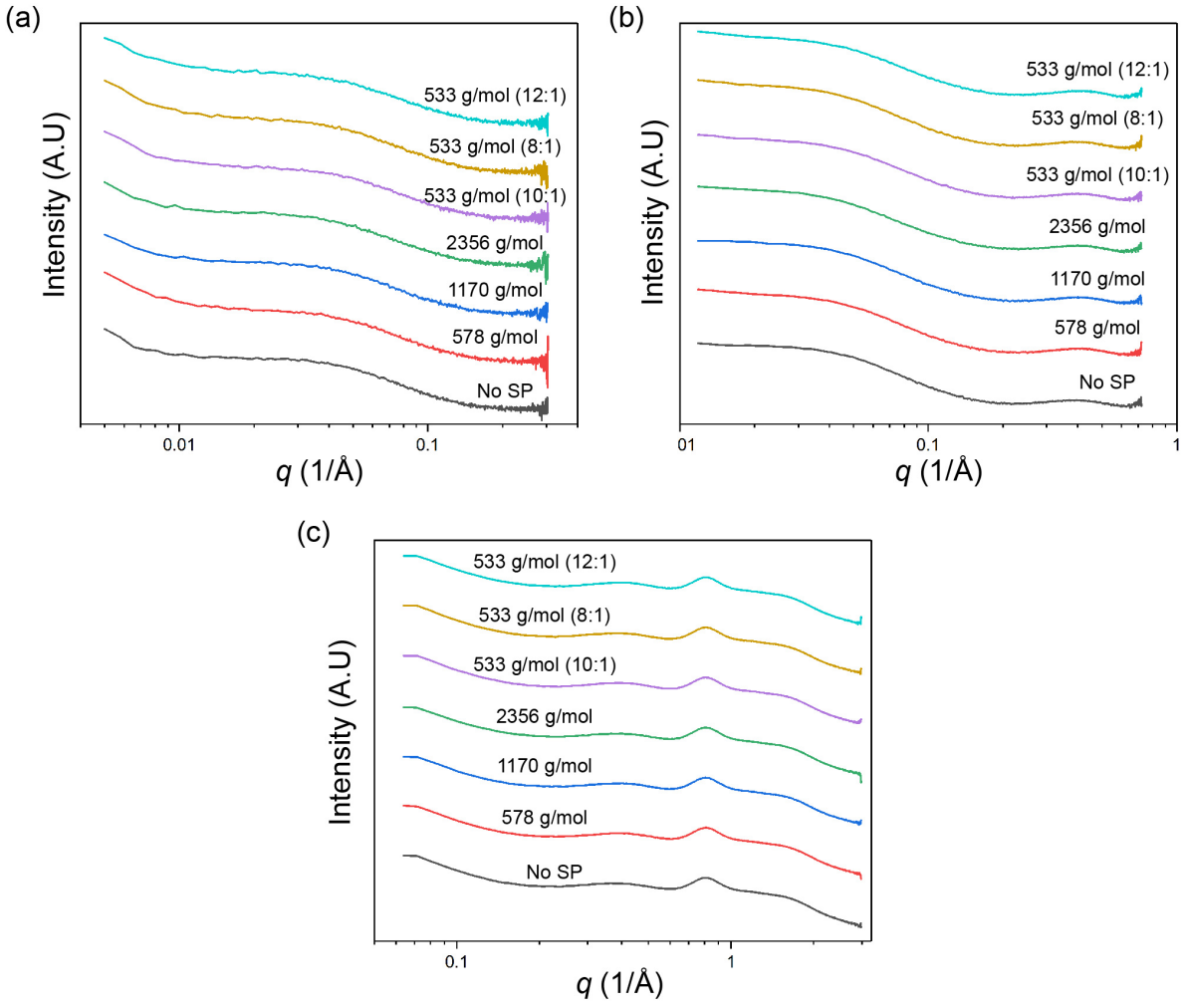


Fig. S2 The results of the X-ray scattering measurements for the PDMS films with SP: (a) SAXS, (b) MAXS, and (c) WAXS data. The spectra were normalized based on the peak intensity and shifted for comparison: as reference peaks, q = 0.0396, 0.400, and 0.829 $Å^{-1}$ were chosen for SAXS, MAXS, and WAXS, respectively. Except for SP with 533 g/mol samples, the base:curing agent ratios are 10:1. For SP with 533 g/mol samples, the ratios are indicated in the figure.

Section D. Nuclear Magnetic Resonance (NMR)

1) SP-incorporated crosslinkers

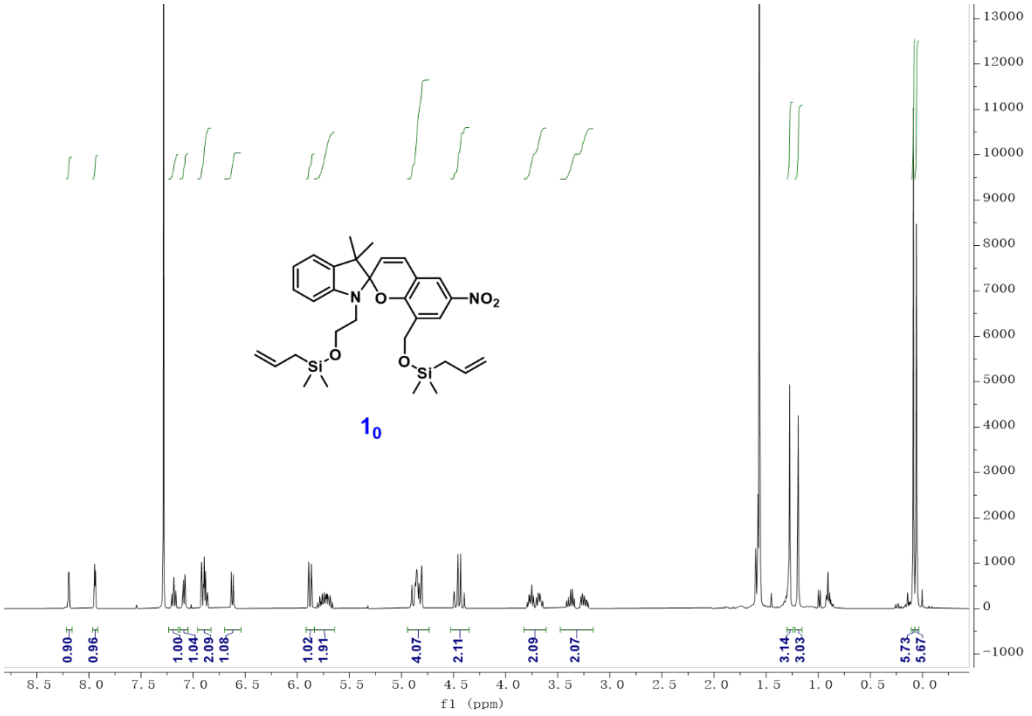


Fig. S3 ^{1}H NMR of **1_0** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

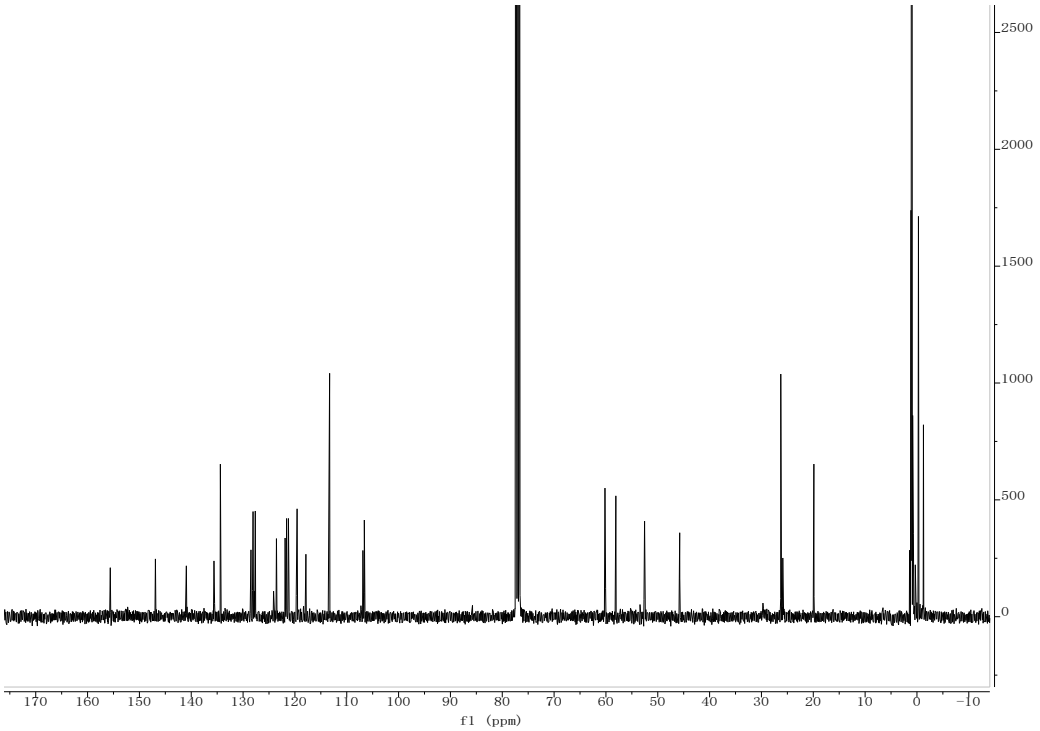


Fig. S4 ^{13}C NMR of **1_0** in $CDCl_3$ (101 MHz, $CDCl_3$, ppm).

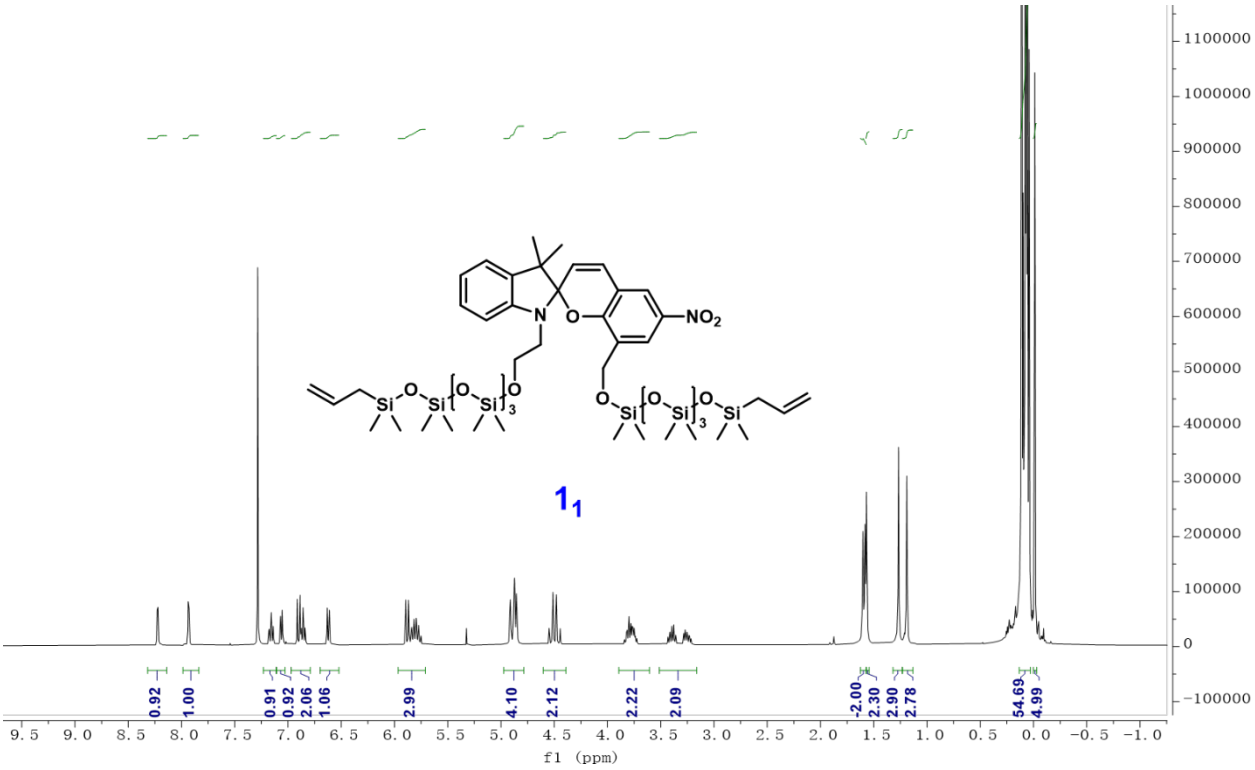


Fig. S5 ^{1}H NMR of **1₁** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

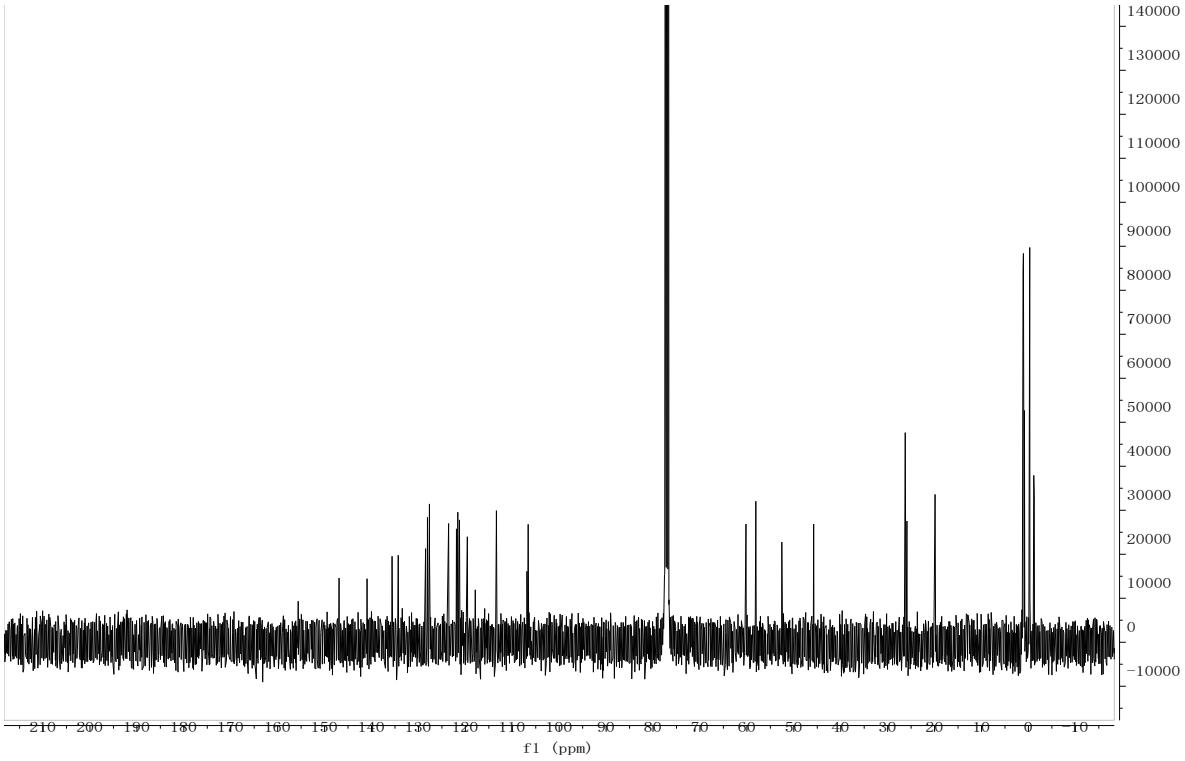


Fig. S6 ^{13}C NMR of **1₁** in $CDCl_3$ (101 MHz, $CDCl_3$, ppm).

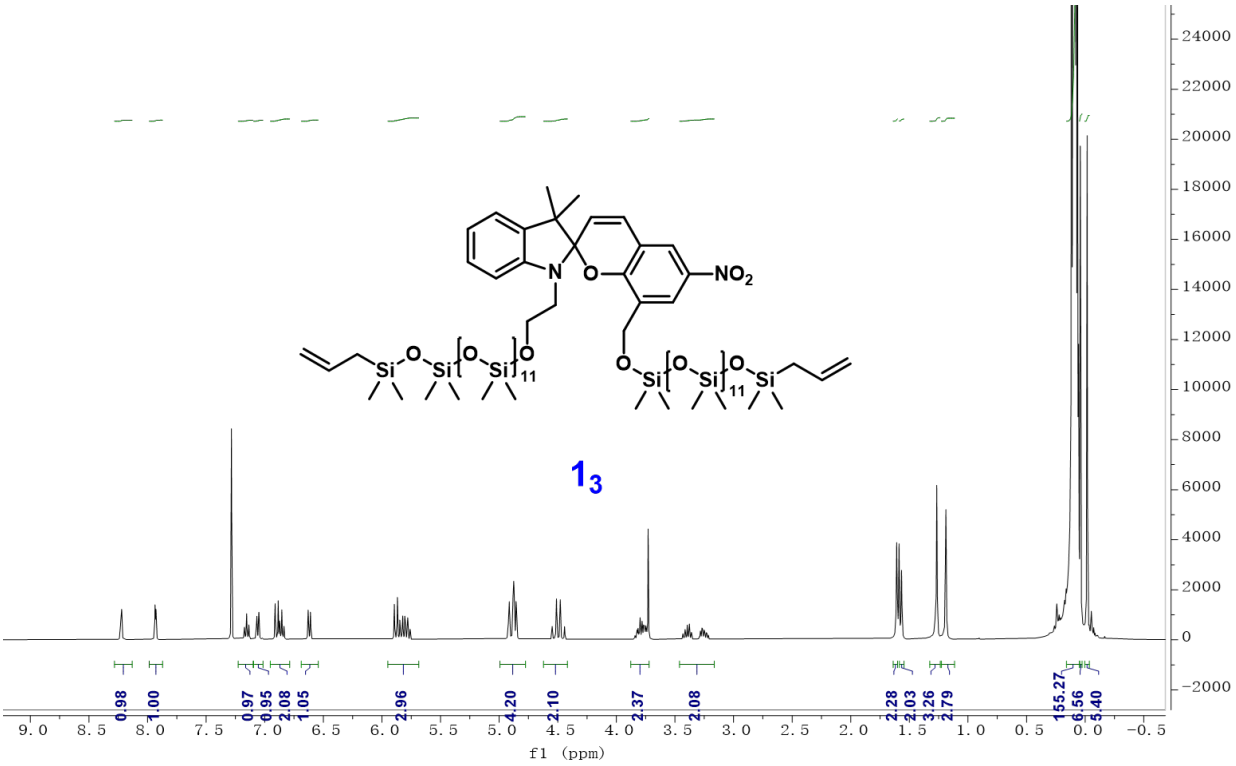


Fig. S7 ^{1}H NMR of **1₃** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

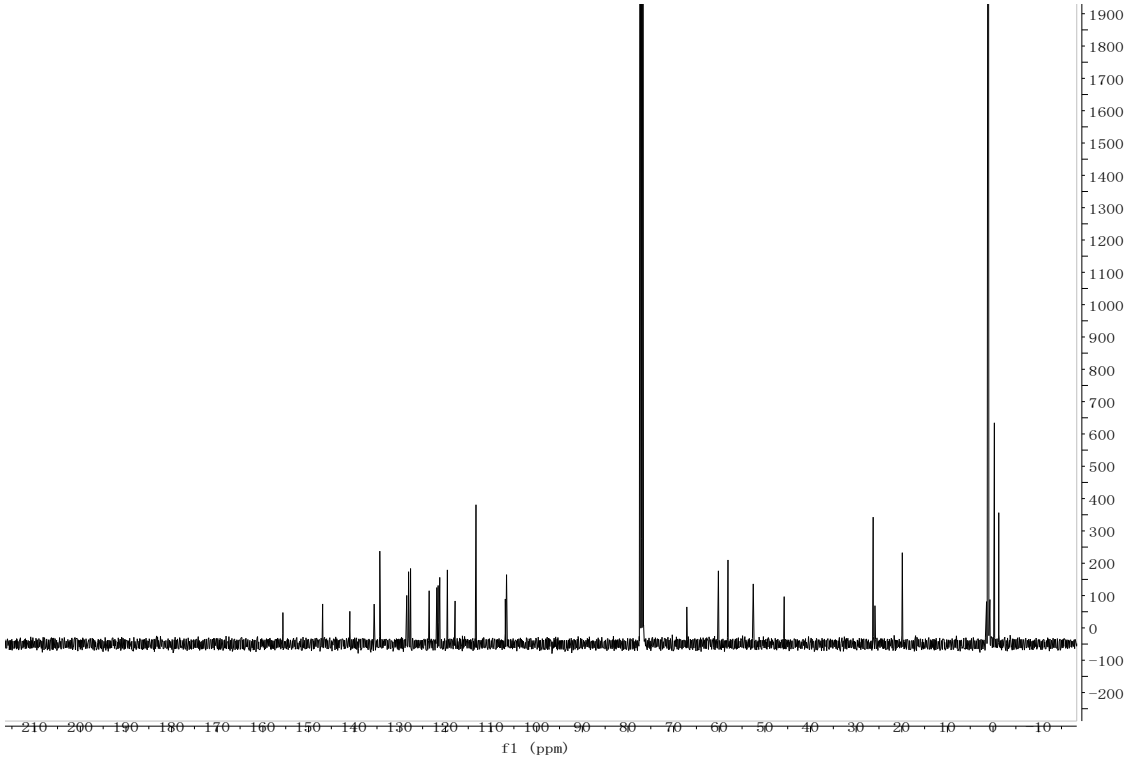


Fig. S8 ^{13}C NMR of **1₃** in $CDCl_3$ (101 MHz, $CDCl_3$, ppm).

2) NMR spectra of intermediates

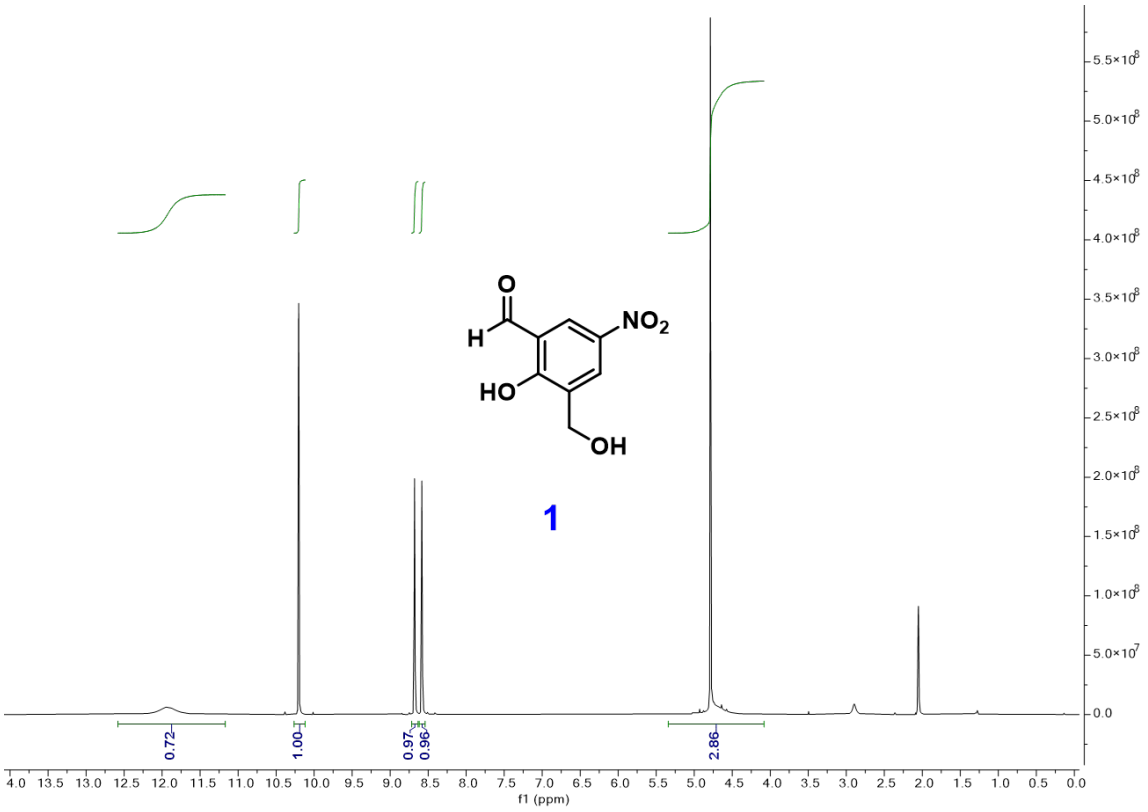


Fig. S9 ^{1}H NMR of **1** in $(CD_3)_2CO$ (500 MHz, $(CD_3)_2CO$, ppm).

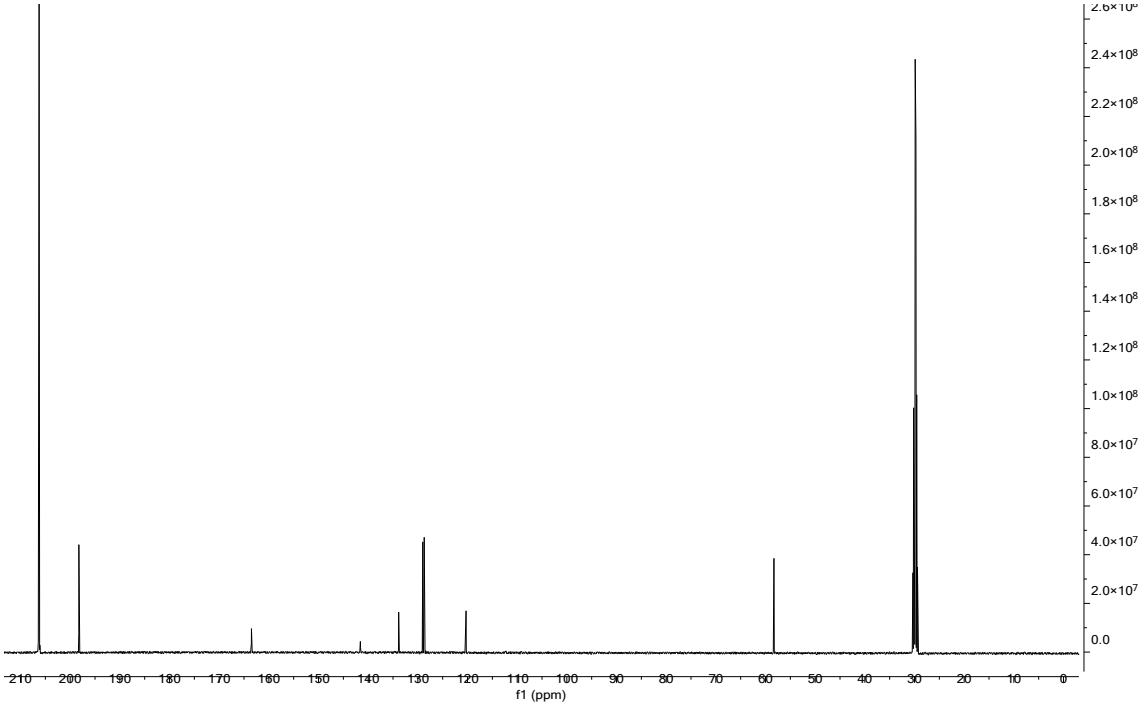


Fig. S10 ^{13}C NMR of **1** in $(CD_3)_2CO$ (126 MHz, $(CD_3)_2CO$, ppm).

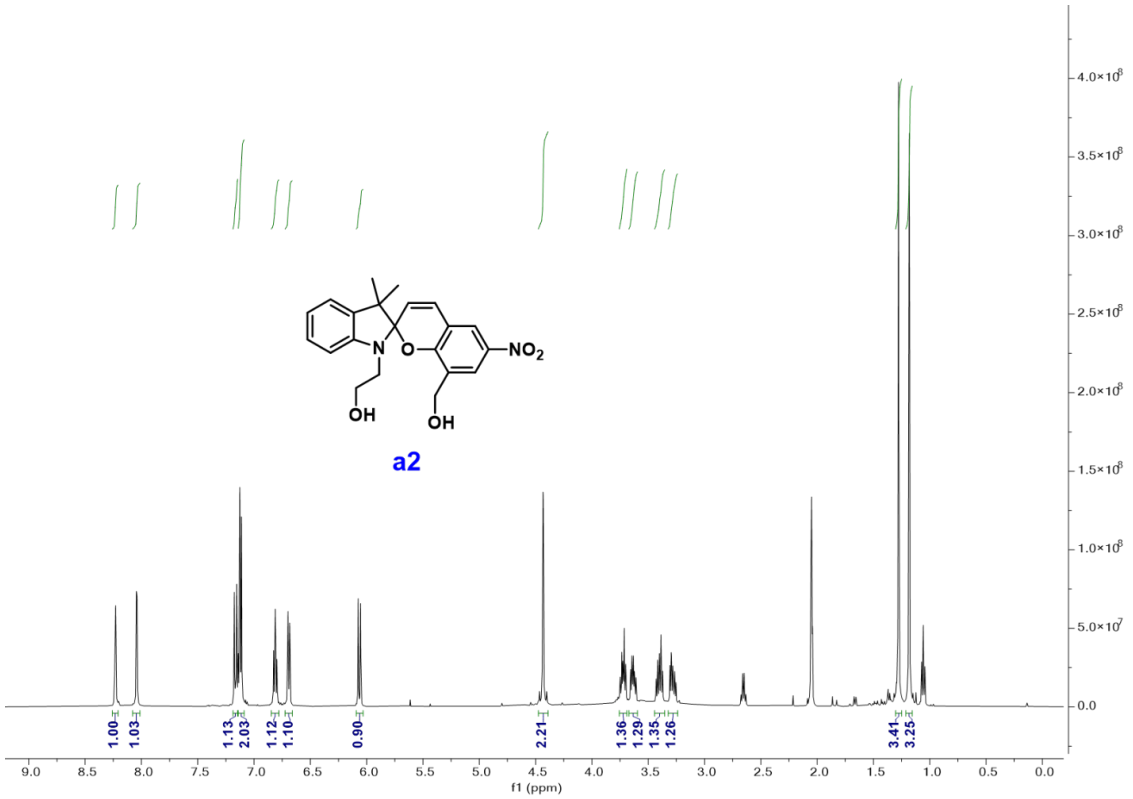


Fig. S11 ^{1}H NMR of **a2** in $(CD_3)_2CO$ (500 MHz, $(CD_3)_2CO$, ppm).

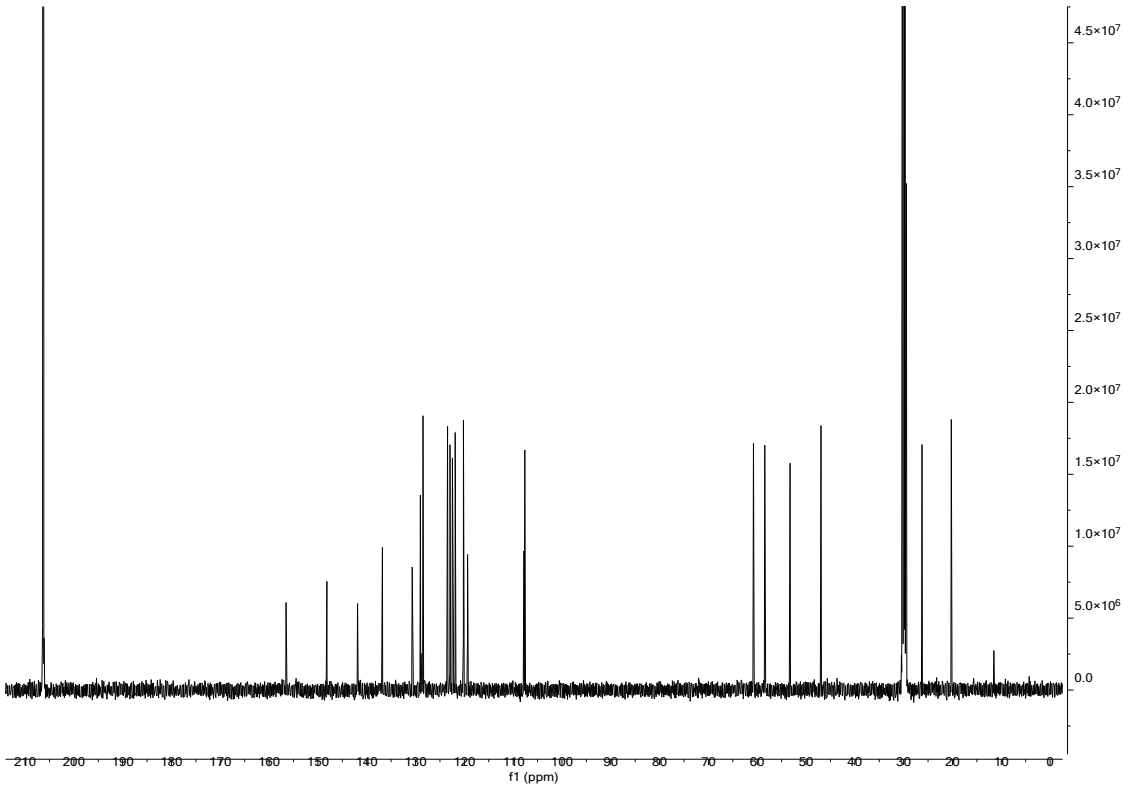


Fig. S12 ^{13}C NMR of **a2** in $(CD_3)_2CO$ (126 MHz, $(CD_3)_2CO$, ppm).

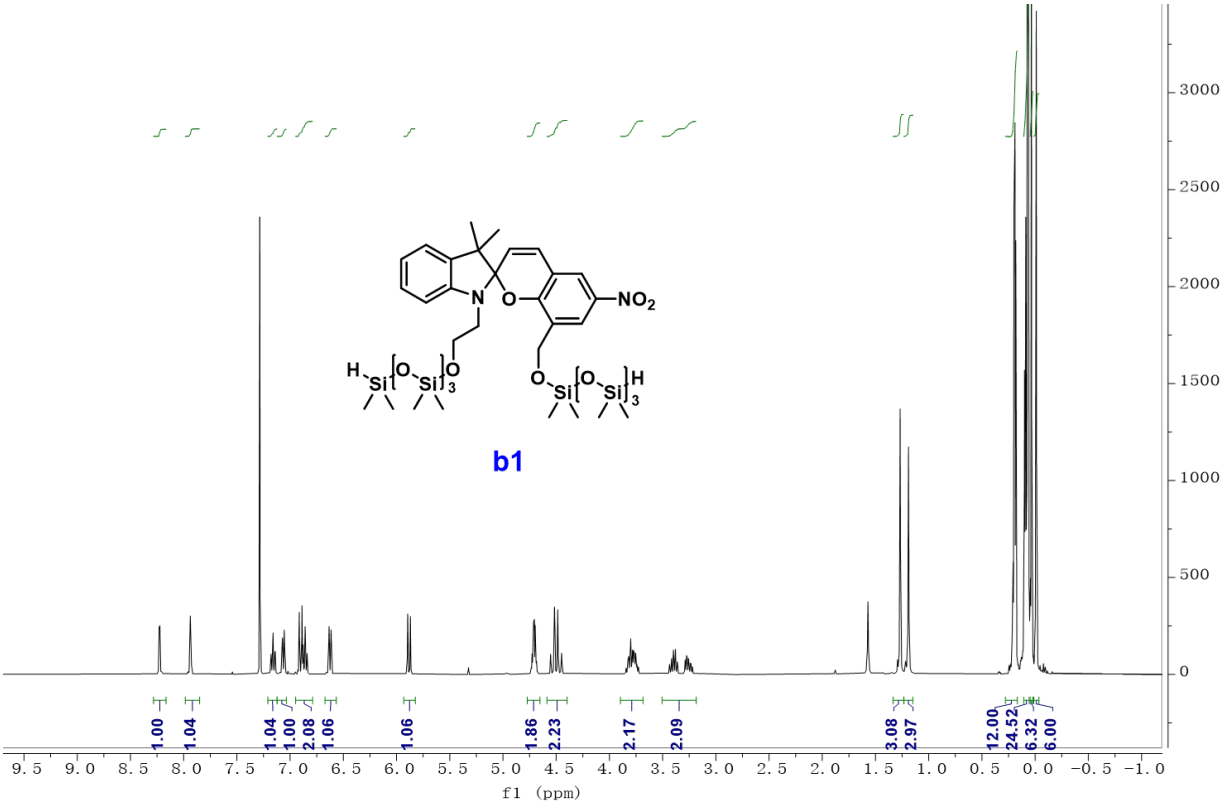


Fig. S13 ^{1}H NMR of **b1** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

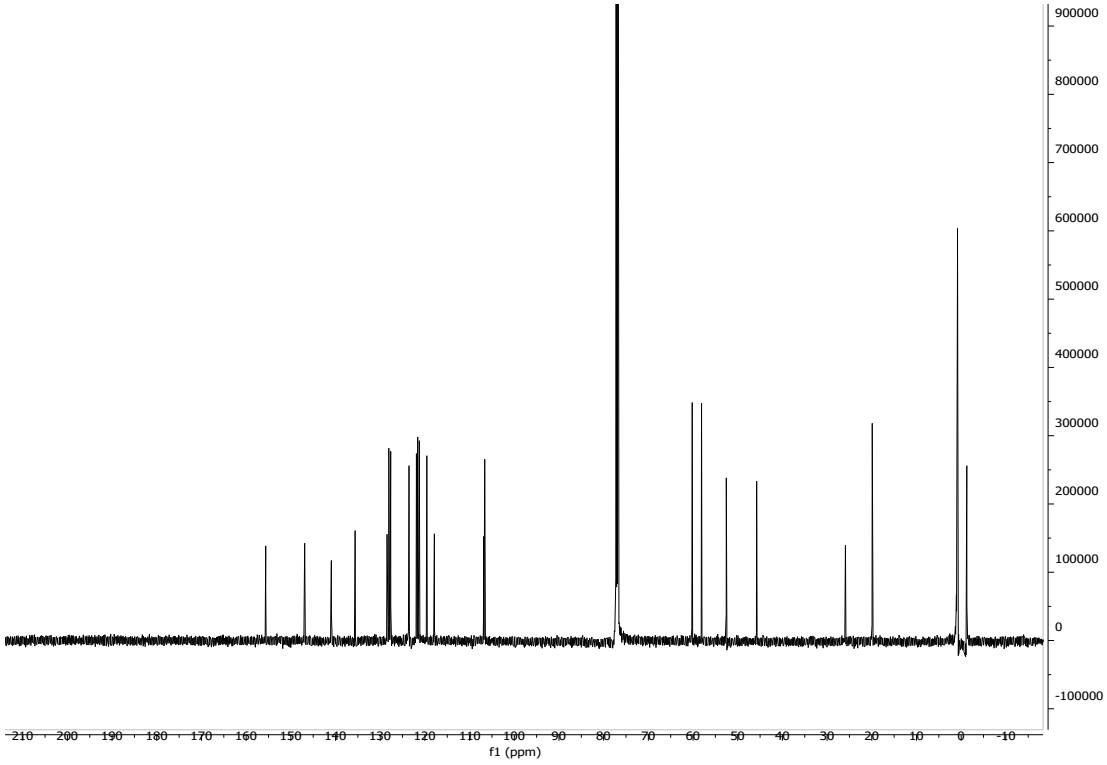


Fig. S14 ^{13}C NMR of **b1** in $CDCl_3$ (151 MHz, $CDCl_3$, ppm).

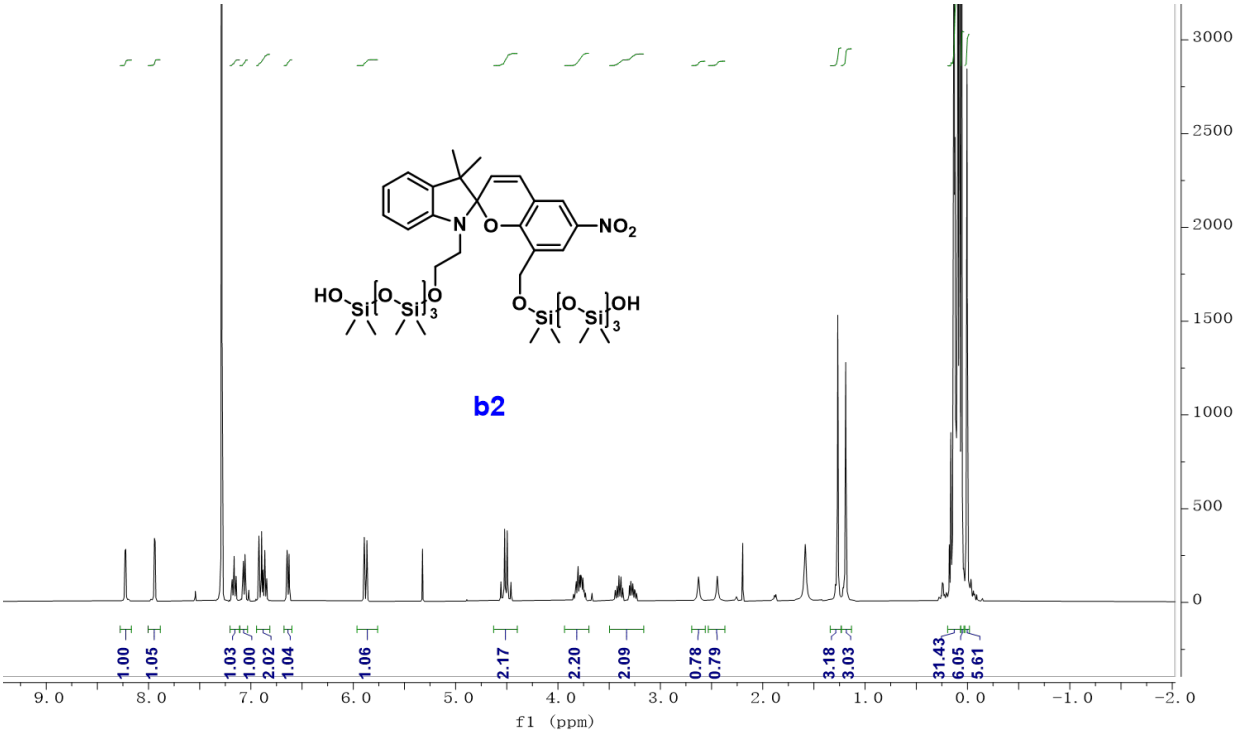


Fig. S15 ^{1}H NMR of crude **b2** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm)

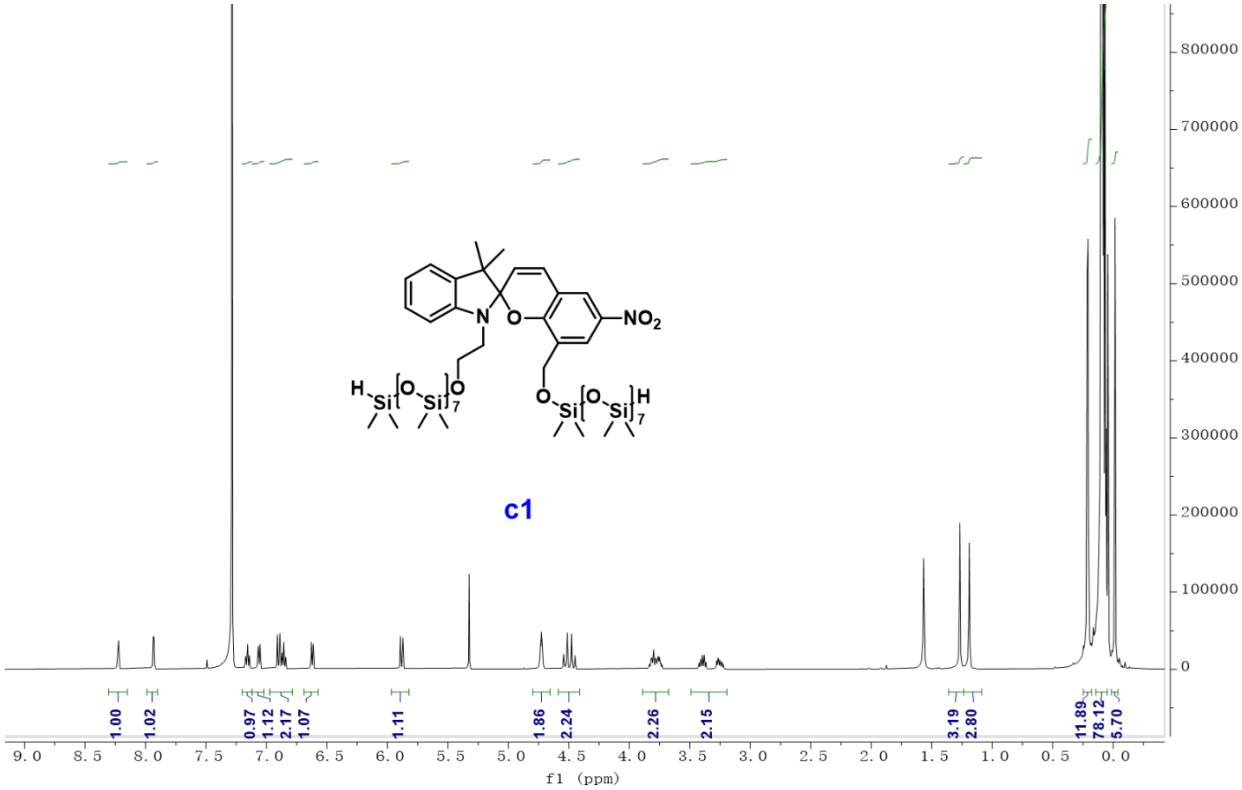


Fig. S16 ^{1}H NMR of **c1** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

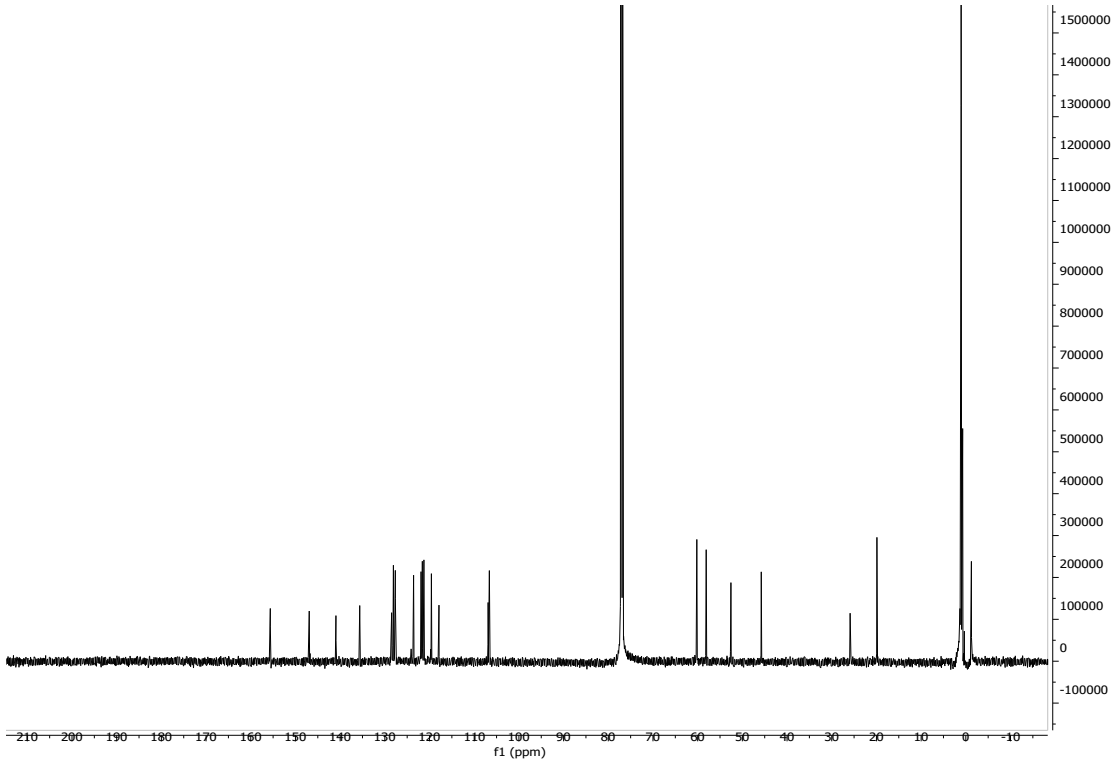


Fig. S17 ^{13}C NMR of **c1** in $CDCl_3$ (151 MHz, $CDCl_3$, ppm).

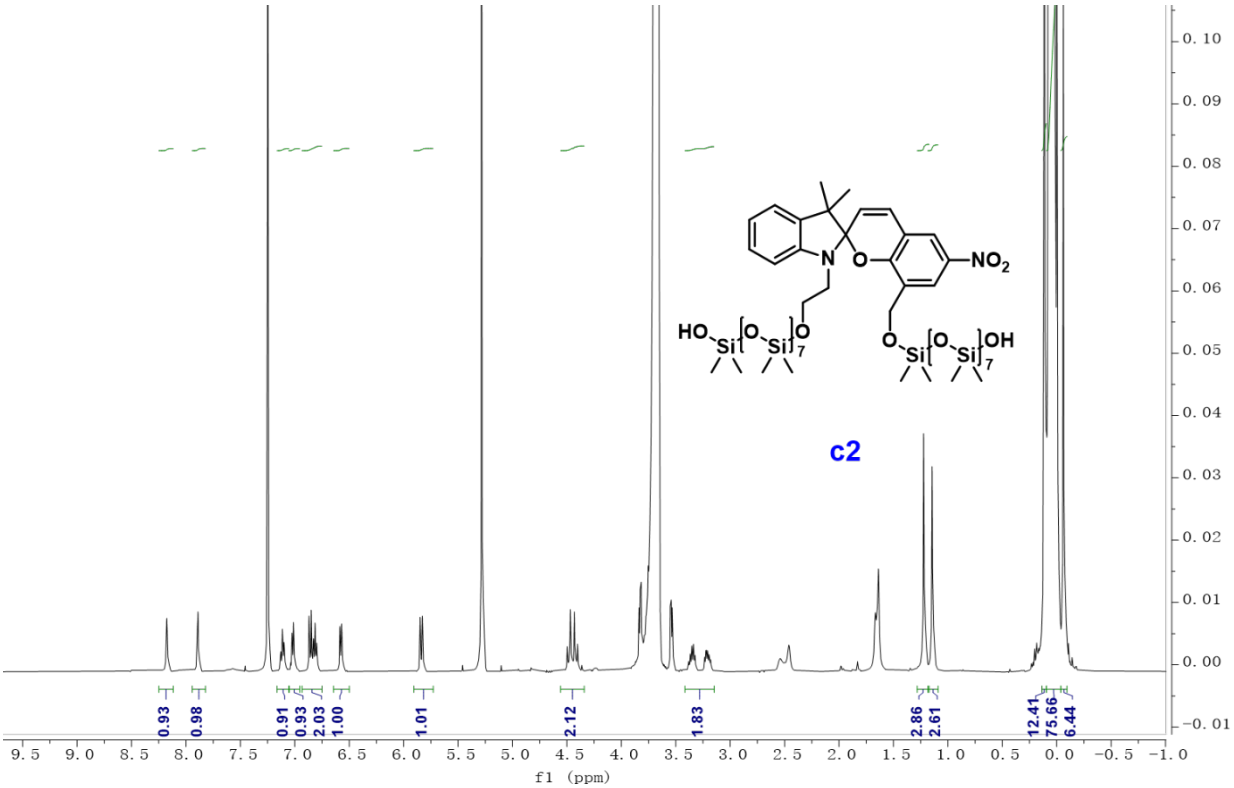


Fig. S18 ^{1}H NMR of crude **c2** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm)

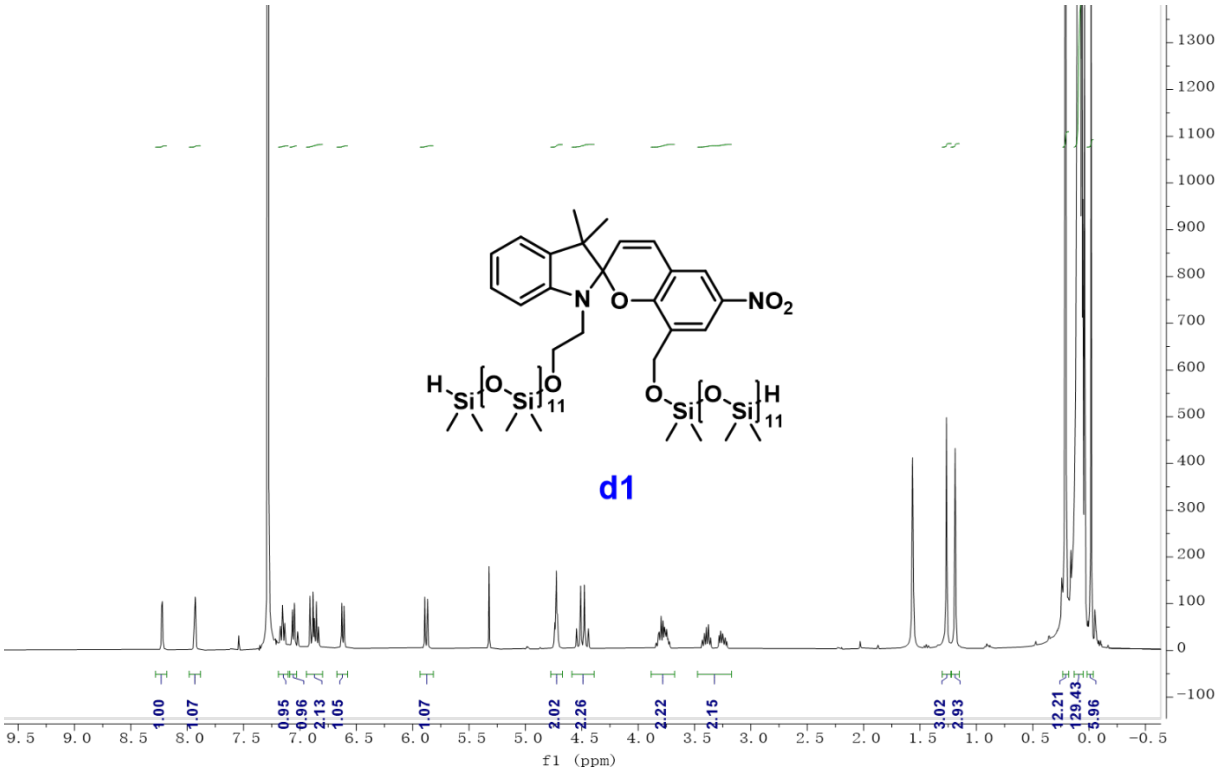


Fig. S19 ^{1}H NMR of **d1** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

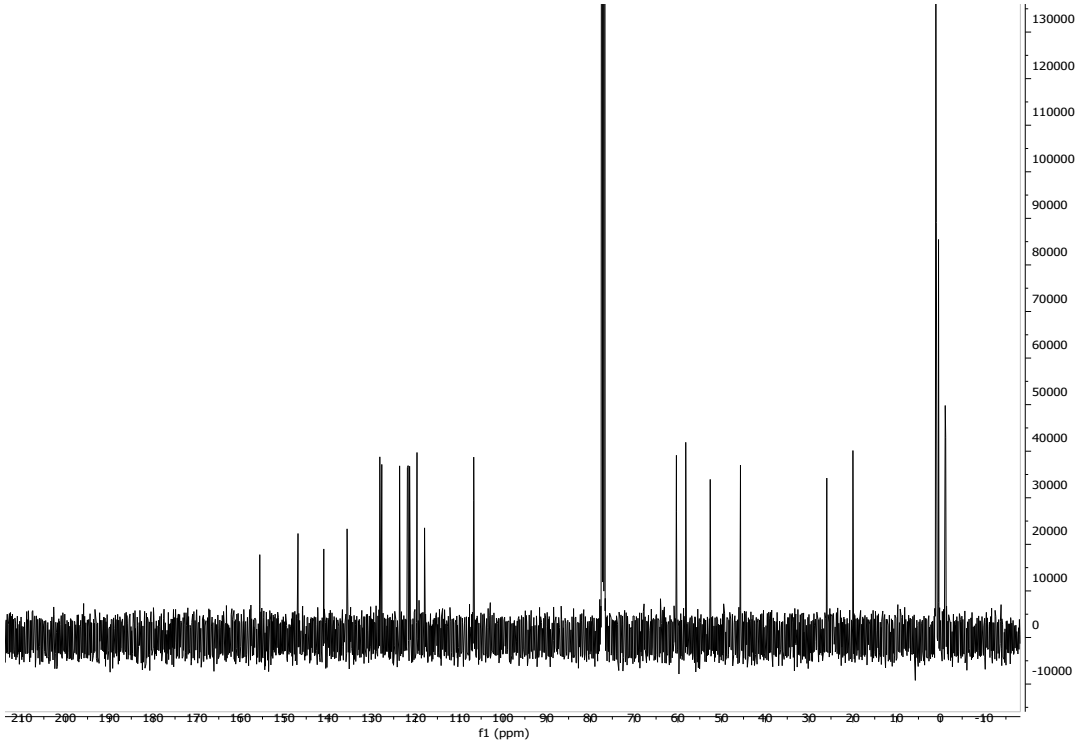


Fig. S20 ^{13}C NMR of **d1** in $CDCl_3$ (101 MHz, $CDCl_3$, ppm).

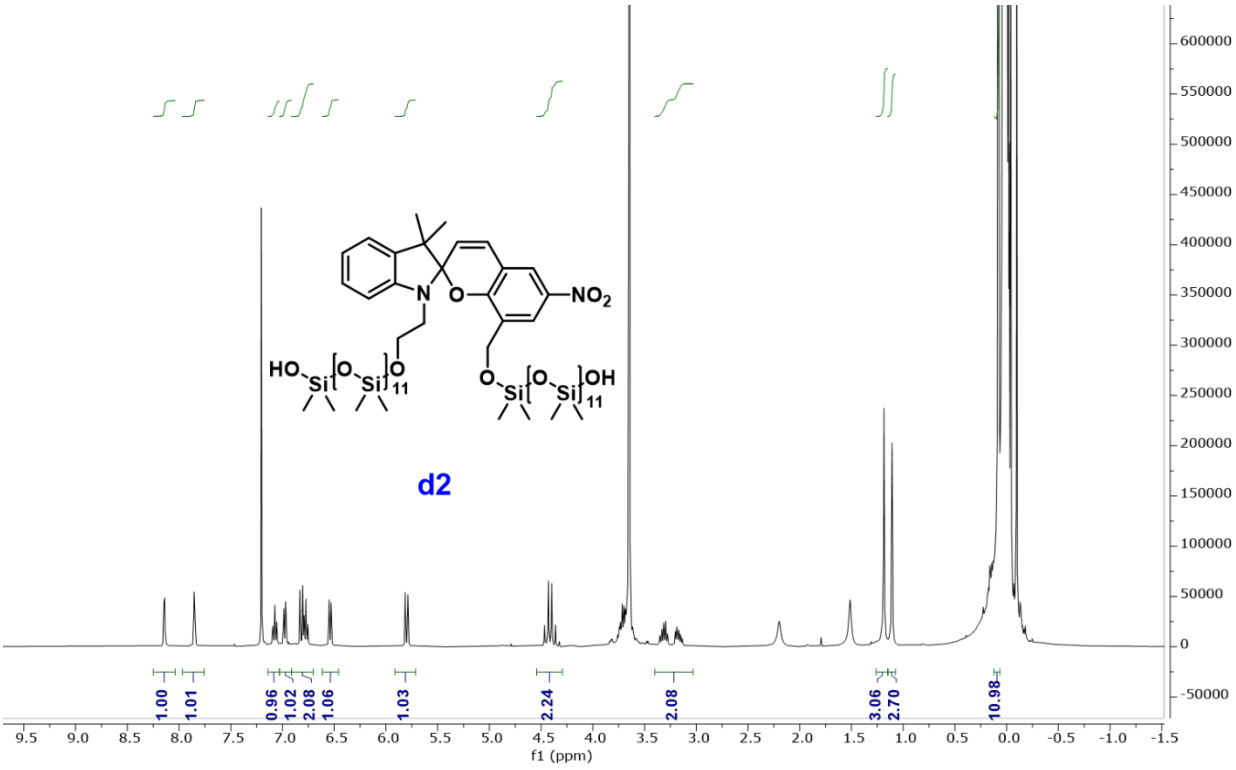


Fig. S21 ^{1}H NMR of **d2** in $CDCl_3$ (400 MHz, $CDCl_3$, ppm).

Section E. Size Exclusion Chromatography (SEC)

1) SEC traces of SP-PDMS-2k (1_3)

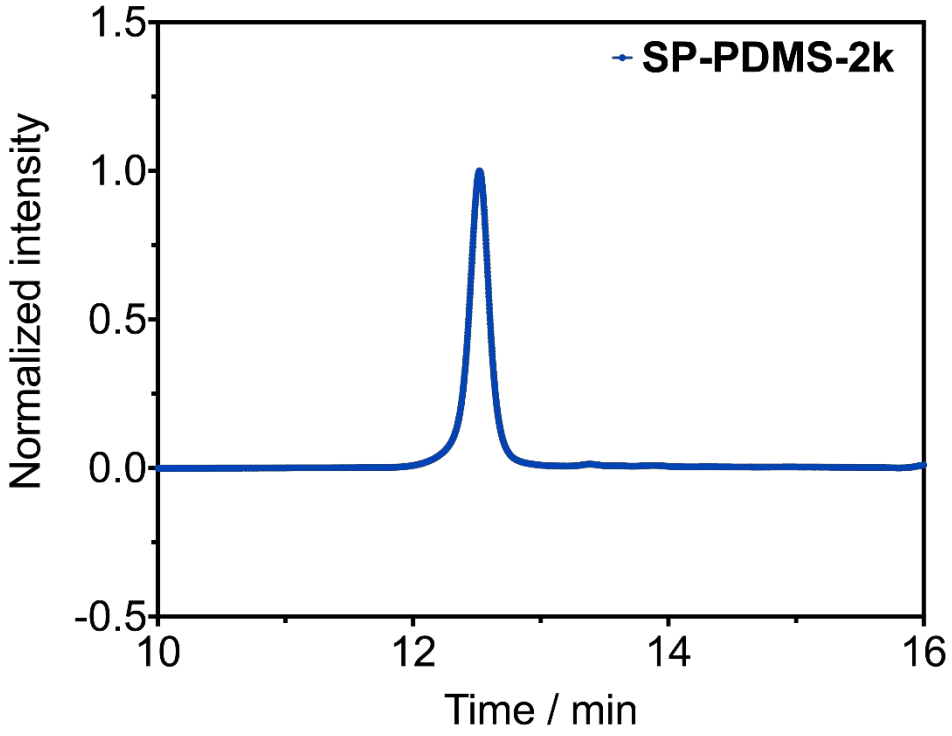


Fig. S22 Extended chloroform SEC trace of **SP-PDMS-2k** (**1_3**) (*M*n = 2347; *Đ* = 1.007).

2) SEC traces of SP-PDMS-1k (1_1)

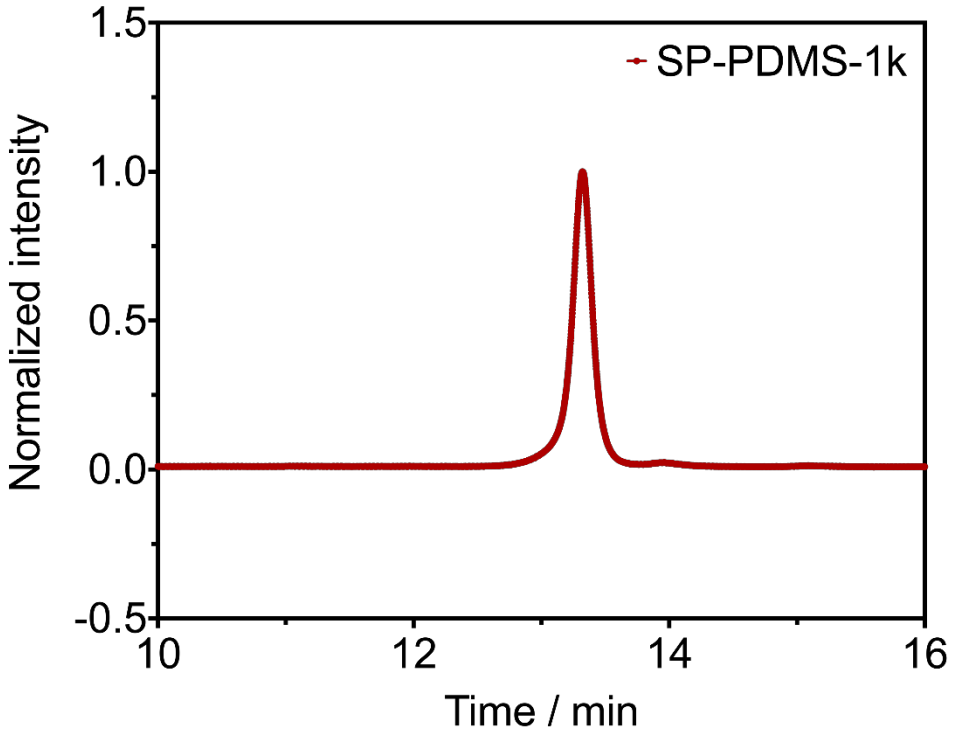


Fig. S23 Extended chloroform SEC trace of **SP-PDMS-1k** (**1_1**) (*M*n = 1201; *Đ* = 1.006).

3) SEC traces of SP-PDMS-500 (1_0)

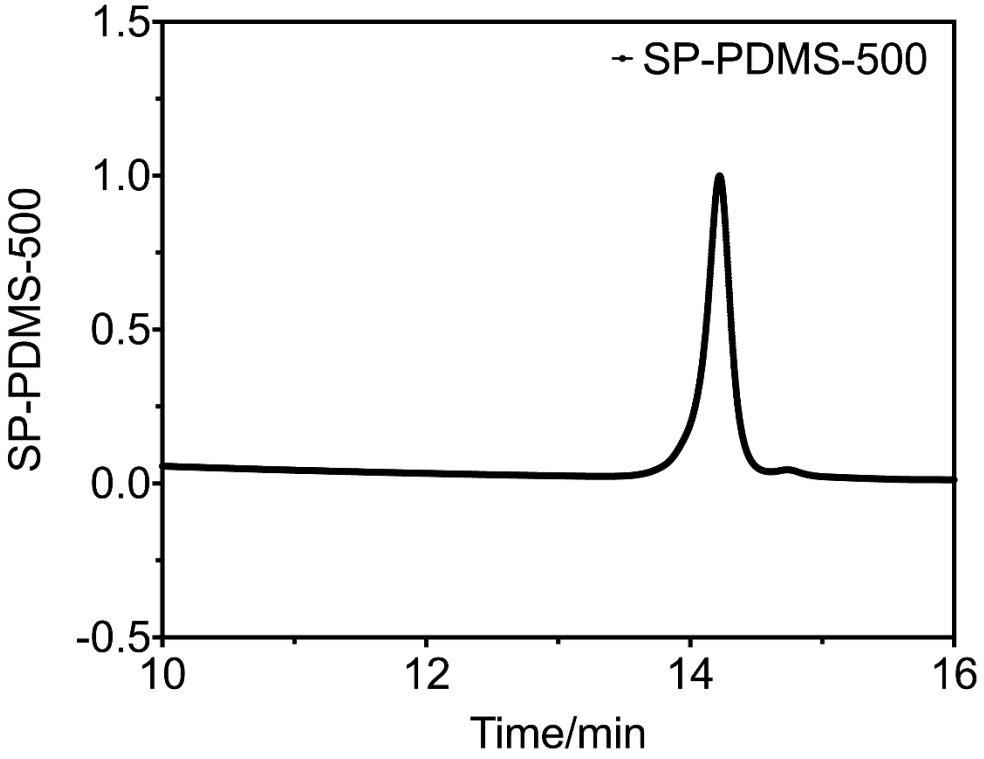


Fig. S24 Extended chloroform SEC trace of **SP-PDMS-500** (**1_0**) (*M*n = 606; *Đ* = 1.008).

Section F. Matrix-assisted Laser Desorption/ionization Time-of-flight Mass Spectrometry (MALDI-TOF-MS)

1) MALDI-TOF of SP-PDMS-2k (1_3)

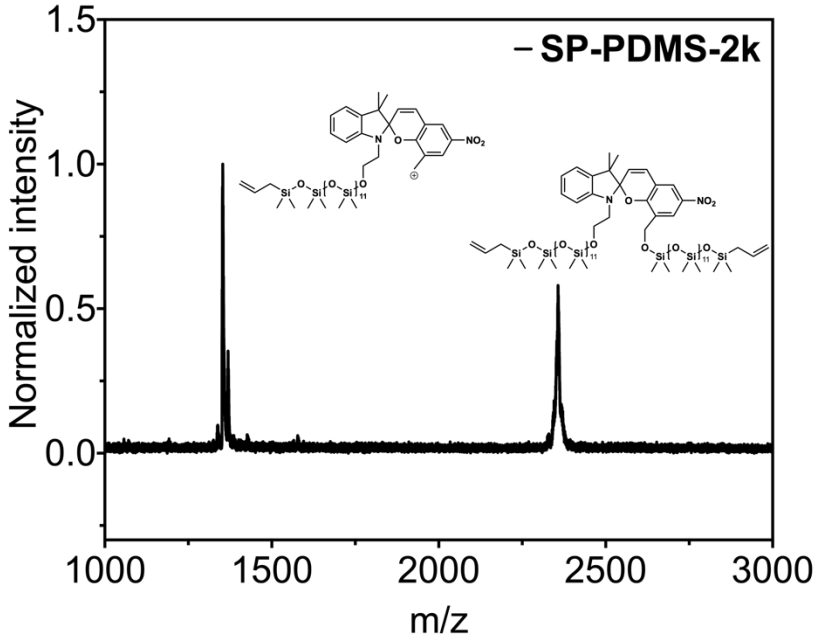


Fig. S25 Full MALDI-TOF spectrum of **SP-PDMS-2k** (**1_3**) (Calcd m/z = 2357.7 [M +H]+; Found m/z: 2357.4 [M + H]+).

2) MALDI-TOF of SP-PDMS-1k (1_1)

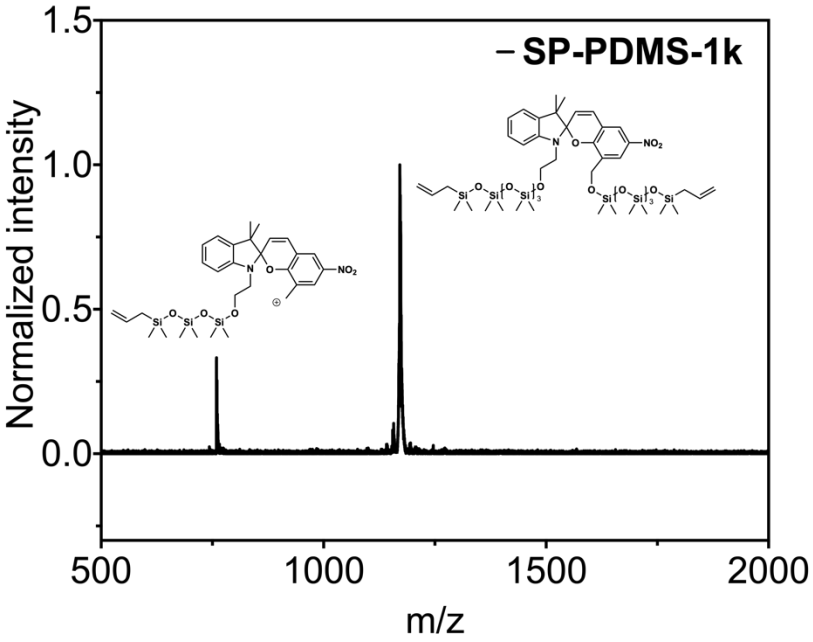


Fig. S26 Full MALDI-TOF spectrum of **SP-PDMS-1k** (1_1) (Calcd m/z = 1170.4 [M +H]+; Found m/z: 1172.3 [M + H]+).

3) MALDI-TOF of SP-PDMS-500 (1_0)

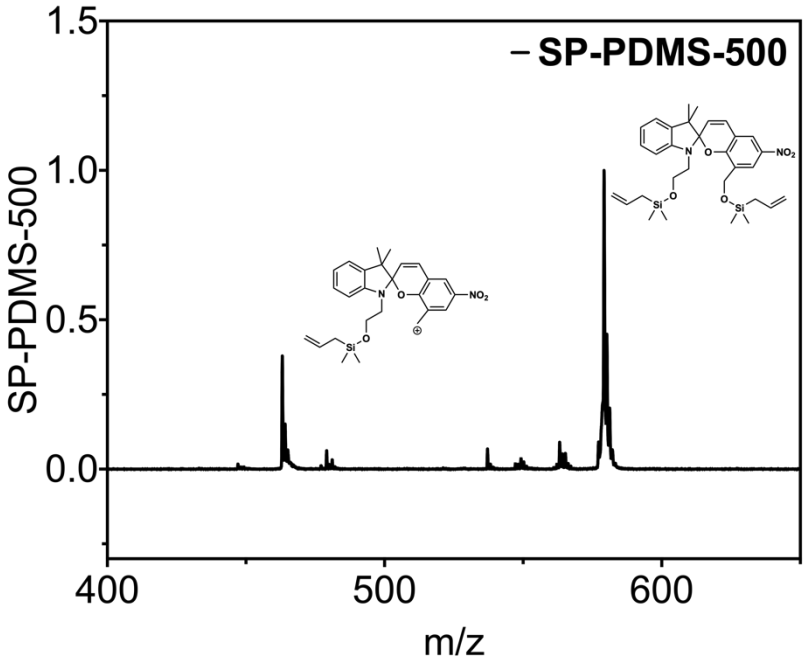


Fig. S27 Full MALDI-TOF spectrum of **SP-PDMS-500** (1_0) (Calcd m/z = 578.3 [M +H]+; Found m/z: 578.8 [M + H]+).

Section G. Estimation of the number of Kuhn lengths for the SP probes

The number of Kuhn length (N) was estimated with the assumptions: (i) the number of Kuhn length in the SP unit is 0 due to its rigid structure, (ii) the molecular weight of Kuhn monomer (M_0) of PDMS is 381 g/mol, and (iii) M_0 of the bis alkane handle (i.e., after the hydrosilylation reaction) is the same as that of polyethylene, 150 g/mol.[5] The estimated values are N = 1.1, 2.6, and 5.7 for $\mathbf{1_0}$, $\mathbf{1_2}$, and $\mathbf{1_3}$, respectively.

Section H. Tensile tests of the PDMS-SP films

1) Procedure for the tensile tests and the RGB analysis

A PDMS sample was cut into a rectangular sample with 3 mm width. Then, the edges of the sample were sandwiched by PDMS films to prevent slipping and carefully attached to the grips of the instrument (TA Instruments, RSA III). The tensile test was performed with the strain speed of 50 %strain/min, and images were taken every ~5 %strain for RGB image analysis to monitor mechanochemical reactions during stretching. For the images, the manual mode was used with the typical setting of exposure time 1/4 sec, F-stop f/5.6, ISO speed ISO-100. During the entire tensile tests, the camera settings and its position were fixed.

Image analysis was conducted with the similar procedure to the previous methods.[1,6,7] The files were saved as CR2 format and imported into Adobe Lightroom Classic CC software. Then, white balance function was applied to all images to standardize. The files were exported as TIFF files and imported into Fiji image J software for further image analysis. Then, each image file was split into red (R), green (G) and blue (B) channels, and mean pixel intensities of each channel in the middle area of the sample were recorded. For each picture, the strains were calculated by measuring the distances between two dots on the samples: $\varepsilon = \frac{Current\ length - Initial\ length}{Initial\ length}$.

2) Normalization of the onset of the mechanochemical reaction by S-S curves

The onset of the mechanochemical reactions (i.e., RGB ratios) was normalized based on stress-strain (S-S) curves. The critical strain (ε_{SH}) was defined as the intersect of the two linear curves before and after the strain-hardening in a S-S curve (Fig. S28), and the strain was normalized as the normalization strain $\bar{\varepsilon} = \frac{\varepsilon}{\varepsilon_{SH}}$. This normalized strain was the measure of how far the sample was stretched from the onset of the strain hardening where some chains start to experience enthalpic distortion.

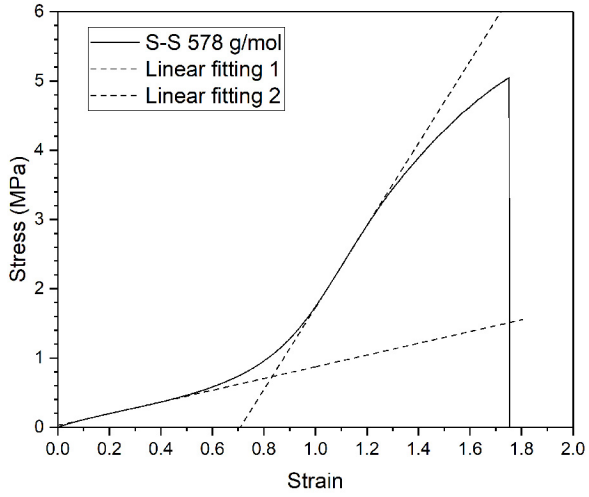


Fig. S28 The determination of the critical strain (ε_{SH}).

Section I. Relaxation kinetics of the PDMS-SP films

1) Procedures for the kinetics measurements using UV-vis

Relaxation kinetics from force-activated MC back to SP under stretching was monitored by UV-vis spectrometer (Photonics, Model 440 UV-Vis Spectrophotometer). A rectangular PDMS sample with 5 mm width was prepared and attached to a handmade stretcher. Here, the edges of the sample were sandwiched with PDMS films to prevent slipping and breaking at the edges. Then, the sample was stretched to the normalized strain of 1.1 ($\bar{\varepsilon} = \frac{\varepsilon}{\varepsilon_{SH}}$), and the isomerization reaction from SP to MC states was monitored under dark condition. After equilibration (30 min), the sample was relaxed to a target normalized strain (e.g., $\bar{\varepsilon_r}$ = 1.1 to 1.0, 0.8, 0.6, 0.4, 0.1), then its relaxation kinetics from force-activated MC back to SP states were monitored under dark condition. In these measurements, data was taken every 10 s.

Relaxation kinetics from photoactivated MC back to SP under no strain was monitored by the UV-vis spectrometer with a similar procedure as above. A rectangular PDMS sample with 5 mm width was mounted onto a handmade stretcher. Then, the sample was irradiated with 380 nm UV LED from 10 cm distance for 15 s, and the relaxation decay was monitored under dark condition with the data interval of 10 s.

2) Determination of the ratios of reaction constants

The analysis on the ratios of the relaxation constants ($\frac{k_{rel}}{k_0}$) is phenomenological. The relaxation curve contains multiple relaxation modes, and we conducted this analysis to capture the effects of the multiple relaxation modes with the following procedure. We expanded/shrank and shifted the relaxation curve at a given normalized strain at relax ($\overline{\varepsilon_r}$) so that the relaxation curve overlaps with a reference relaxation curve. In this study, we choose the relaxation curve at $\overline{\varepsilon_r}$ = 0.1 as a reference curve with k_0. For y axis, we expanded/shrank (i.e., multiplying with constant α) and shifted (i.e., adding constant γ). For x axis, we only expanded/shrank the curve by a factor of constant $\beta = \frac{k_0}{k_{rel}} = t_{rel}$. The ratio of the relaxation constants ($\frac{k_{rel}}{k_0}$) was obtained by finding parameters α, $\beta = \frac{k_0}{k_{rel}} = t_{rel}$, and γ, that make a target relaxation curve overlap with the refence curve. It is noted that both the expansion/shrinkage in y direction and the shift in y direction do not affect the relaxation constant. To capture an initial large decay, the analysis was conducted with the ranges that cover 95% of the initial decay of the reference curves (i.e., > $3\tau_{ref}$): 0 - 500 s for **SP-PDMS-500** (**1_0**) and 0 – 250 s for **SP-PDMS-1k** (**1_1**) and **SP-PDMS-2k** (**1_3**) cases.

The calculated $\frac{k_{rel}}{k_0} = \frac{1}{\beta}$ are summarized in Fig. 7a for the force activated MC back to SP cases. Table S2 summarizes the comparison between the decays of UV activated MC and force activated MC cases. It summarizes the ratios of reaction constant (k_{rel}) to that of the fore activated MC to SP inside the PDMS film incorporating SP of *M*n = 578 g/mol at $\overline{\varepsilon_r}$ = 0.1 ($k_{0\ for\ 578}$). The results show that $\frac{k_{rel}}{k_{0\ for\ 578}}$ of force activated and UV activated cases are almost the same at a given molecular weight, indicating that the force probes feel little tension at $\overline{\varepsilon_r}$ = 0.1. Also, $\frac{k_{rel}}{k_{0\ for\ 578}}$ becomes larger as the molecular weight of the SP force probes increases. This indicates that local environments of the force probes are different and become less polar around SP with a longer molecular weight.

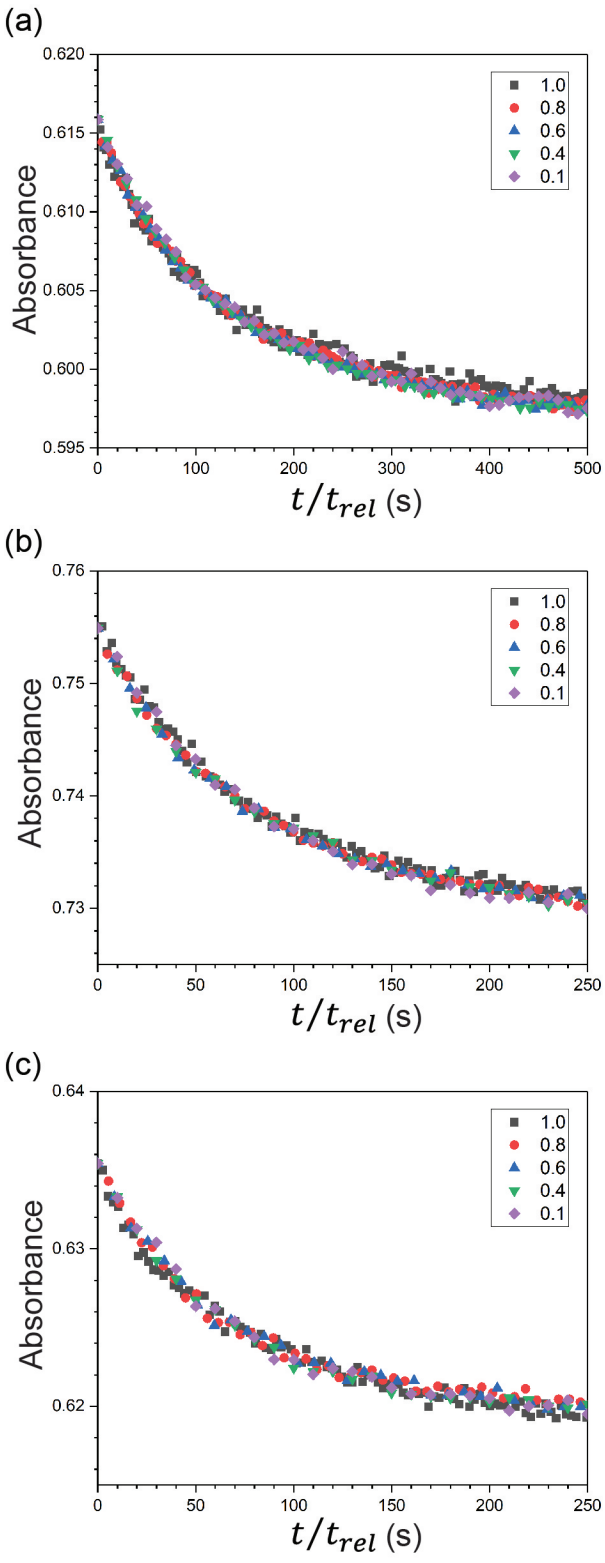


Fig. S29 Representative overlapped relaxation curves for the determination of the reaction constant ratios: (a) **SP-PDMS-500** ($\mathbf{1_0}$) case, (b) **SP-PDMS-1k** ($\mathbf{1_1}$) case, and (c) **SP-PDMS-2k** ($\mathbf{1_3}$) case.

Table S2 The reaction constant ratio ($\frac{k_{rel}}{k_{0\ for\ 578}}$) of force activated and UV activated MC back to SP inside PDMS films[a)]

	$\frac{k_{rel}}{k_{0\ for\ 578}}$		
	578 g/mol	1170 g/mol	2356 g/mol
PDMS film at $\bar{\varepsilon_r} = 0.1$	1.00	1.95	2.35
PDMS film with UV activation	1.07	1.82	2.24

a) $k_{0\ for\ 578}$ is the reaction constant of the PDMS film incorporating SP with *M*n = 578 g/mol at $\bar{\varepsilon_r}$ = 0.1 and is used as a reference for comparison.

Section J. Fitting with the Gent model

To obtain limiting extension ratio (λ_m), we fitted the initial portions of the stress (σ) - strain (ε) curves in Fig. 5 with the following constitutive equation proposed by Gent that takes into account of strain hardening[8,9] (the strain in Fig. 5 was converted to an extension ratio (λ) by $\lambda = 1 + \varepsilon$):

$$\sigma = \frac{E(\lambda - \frac{1}{\lambda^2})}{3(1 - \frac{J}{J_m})}$$

E is the Young's modulus. Under the uniaxial condition, $J = \lambda^2 + \frac{2}{\lambda} - 3$, and $J_m = \lambda_m^2 + \frac{2}{\lambda_m} - 3$. Here, we chose E and J_m as the fitting parameters and obtained λ_m. The fitting results are summarized in Table S3.

Table S3 The summary of the fitting results

	Young's modulus (MPa)	λ_m
PDMS/SP-PDMS-500 (**1**$_0$)	0.95	2.39
PDMS/SP-PDMS-1k (**1**$_1$)	1.06	2.29
PDMS/SP-PDMS-2k (**1**$_3$)	1.11	2.28

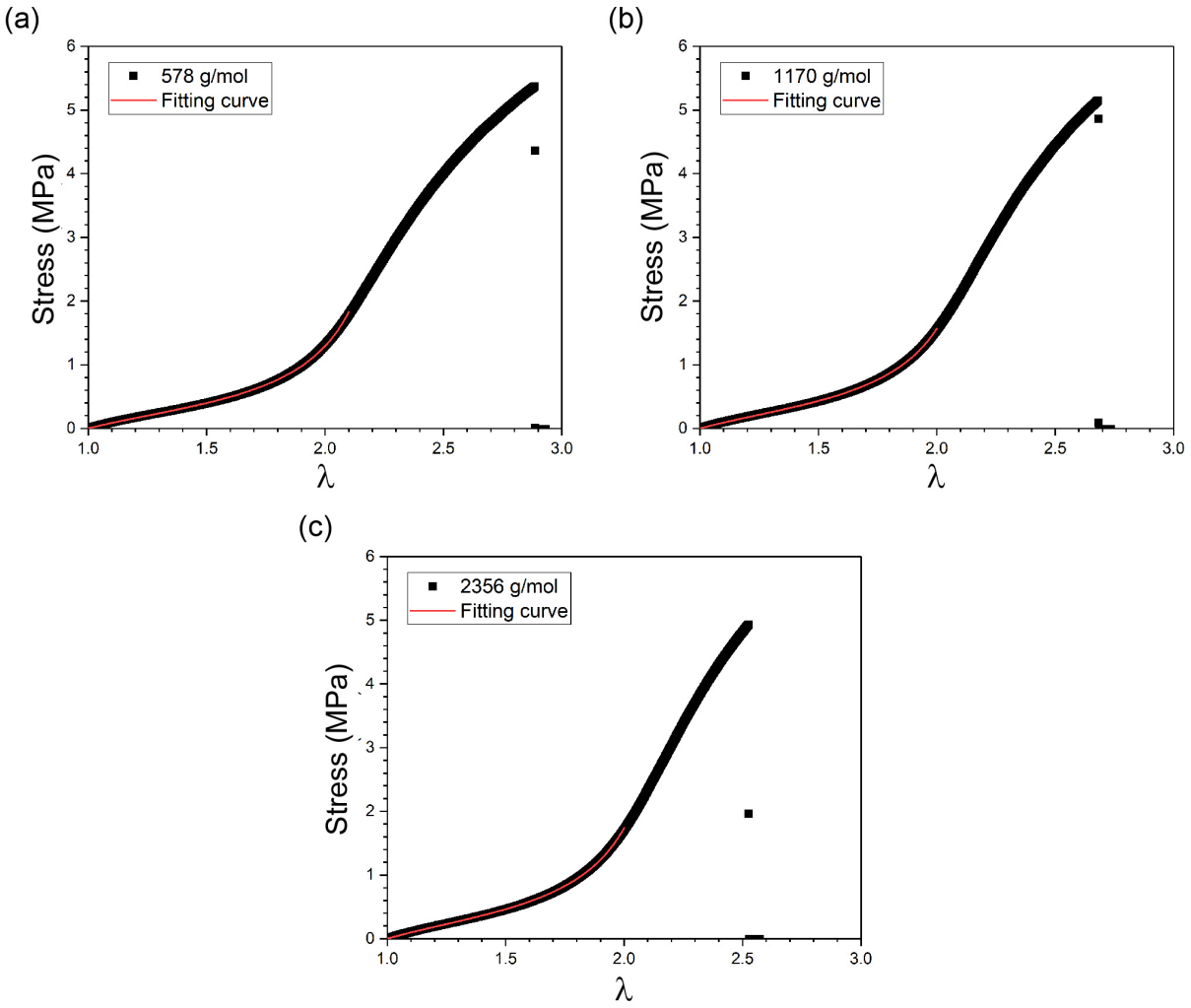


Fig. S30 Representative fitting results: (a) SP-PDMS-500 (1_0) case, (b) SP-PDMS-1k (1_1) case, and (c) SP-PDMS-2k (1_3) case.

Section K. References

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