Supporting Information for

Supramolecular polymer networks crosslinked by crown ether-based host–guest recognition: dynamic materials with tailored mechanical properties in bulk

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Materials and methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Monomer **2**[S1], compounds **4**[S1], **5**[S2] and **6**[S3] were prepared according to the established methods. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{1}H and ^{13}C NMR chemical shifts were reported relative to residual solvent signals. High resolution mass spectra were obtained on a Bruker SolariX 7.0T FT-ICR MS spectrometer. Gel permeation chromatograph (GPC) was obtained by an HLC-8320 GPC (TOSOH, Japan) instrument using dimethylformamide (DMF) as eluent with polystyrene standards. The thermal stability analysis was conducted using a TA Instruments Q500 thermogravimetric analyzer (TGA) under the nitrogen. Each sample (~5 mg) was heated from 50 to 800 °C with a rate of 20 °C/min. Transition temperatures of materials determined on a TA Instruments Q2000 differential scanning calorimetry (DSC) under the nitrogen.

Mechanical tests: The mechanical properties of the SPNs-**1**−**5** samples were measured using an Instron 3343 machine in standard stress/strain experiments at room temperature with a strain rate of 100 mm/min. The samples for the tensile tests were in a rectangle shape [20 mm (length) × 0.5 mm (width) × 0.3 mm (thickness)]. Cyclic tensile tests with different applied deformations (from 50 to 400%) were performed based on eight specimens. Cyclic tensile tests for the recovery experiments were performed with a predefined 300% strain at a deformation rate of 100 mm/min. The tests were based on one specimen with the rest intervals of 0, 0.5, 1, 2, and 3 h, respectively. Rheological experiments were carried out using a TA Instruments ARES G2 stress-controlled rheometer with a 20 mm parallel plate attachment. The disk-shaped SPN-**5** film with a thickness of 0.5 mm and diameter of 8 mm was pressed to the sandblasted parallel plate with a force of 5 N to avoid slippage. Cyclic temperature sweeps were performed from 40 to 100 °C with a heating rate of 5 °C/min under the frequency of 1.0 rad/s. Dynamic oscillatory frequency sweeps from 0.05 to 100 rad/s. Stress relaxation measurements were carried out under the strain amplitude 5% at 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, respectively. Master curves of storage modulus (G') and loss modulus (G'') were obtained by time-temperature superposition shifts at a reference temperature of 30 °C. Based on the Arrhenius plot of temperature-dependent shift factors, apparent activation energy (E_a) was calculated from the slope of the curve.

pH-responsiveness experiments: The SPN-**5** sample [rectangle, 20 mm (length) × 0.5 mm (width) × 0.3 mm (thickness)] was dissolved in DCM, and 1 eq. of TEA was added. The mixture was stirred at room temperature for 1 h. Then, MeOH was added to collect the polymer as precipitate. After vacuum drying, tensile test was performed. Subsequently, 0.5 and 1 eq. of TFA were added to the TEA treated sample solution in acetone, respectively. The mixture was stirred at room temperature for 1 h. A saturated aqueous solution of NH_4PF_6 solution was added, and precipitate was formed which was isolated and dried under vacuum 12 h. The specimens used for the tensile tests underwent hot-pressing at 80 °C for 10 min in the mold with a rectangle shape [20 mm (length) × 0.5 mm (width) × 0.3 mm (thickness)]. The tensile tests of the two samples were performed at room temperature with a strain rate of 100 mm/min, respectively.

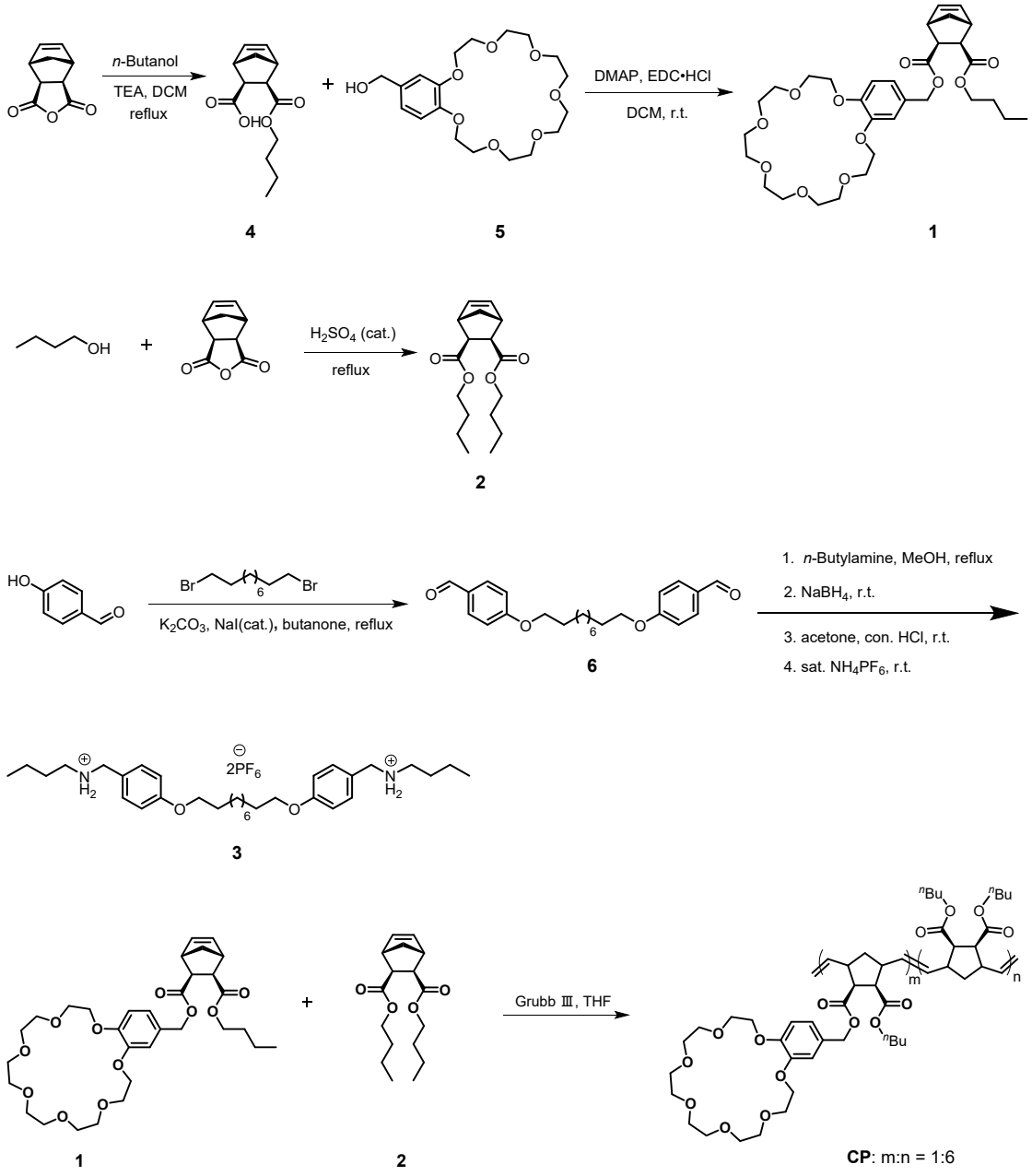
Self-healing experiments: The SPN-**5** sample [dumbbell shape, 20 mm (length) × 0.3 mm (thickness)] was cut into two pieces. The cut faces were gently pressed together. And then, the sample was placed in a vacuum drying oven to keep the environment temperature at 60 °C for various healing times. Finally, tensile tests with a strain rate of 100 mm/min were performed on the healed samples. During the self-healing process, no solvents were added. The self-healing efficiency was evaluated by the ratio of tensile strength of the pristine sample to that of the healed sample.

Reprocessing experiments: The SPN-**5** sample [dumbbell shape, 20 mm (length) × 0.3 mm (thickness)] was cut into small pieces, and then the chippings were remolded by hot-pressing in a Teflon mold. The tensile test of the remolded sample was performed at room temperature with a strain rate of 100 mm/min. Such a procedure was repeated for 3 times to obtain corresponding stress−strain curves.

Preparation of SPNs

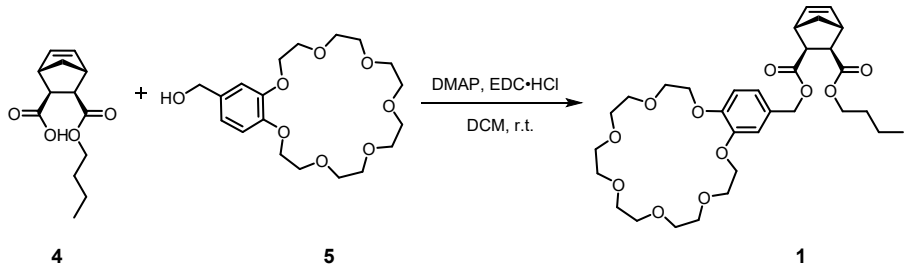
The SPNs were constructed with CP and cross-linker (10:1, 10:2, 10:3, 10:4, 10:5 molar ratio, B21C7 moiety/DAAS-based cross-linker). The CP (200 mg) was dissolved in 3 mL DCM. Then the cross-linker was added. The mixture was stirred at room temperature for 2 h. The solvent was evaporated at 40 °C. The samples were maintained at 60 °C for 24 h in vacuo for annealing purposes. Afterwards, the samples underwent hot pressing at 80 °C for 10 min in the mold. Upon cooling, the target SPNs-**1**−**5** were obtained and used for various tests.

Synthesis of compounds 1, 2, 3 and CP



Scheme S1. Synthetic route to compounds **1**, **2**, **3** and CP.

Synthesis of compound 1



4 **5** **1**

Compound **4** (1.96 g, 8.17 mmol), EDC·HCl (1.57 g, 8.17 mmol), and DMAP (0.30 g, 2.45 mmol) were dissolved in DCM (70 mL). Compound **5** (3.47 g, 8.99 mmol) was added. The mixture was stirred at room temperature overnight and purified via gel chromatography to afford monomer **1** as a colorless oil (3.47 g, 70%). The ^{1}H NMR spectrum of compound **1** is shown in Figure S1. ^{1}H NMR (CD_3CN, 298 K, 400 MHz) δ (ppm): 6.95 (s, 1H), 6.91 (br, 2H), 6.23 (s, 2H), 5.04 (d, J = 12.0 Hz, 1H), 4.92 (d, J = 12.0 Hz, 1H), 4.16−4.09 (m, 4H), 4.03−3.97 (m, 1H), 3.87−3.76 (m, 5H), 3.66−3.63 (m, 4H), 3.62−3.58 (m, 4H), 3.57 (d, J = 1.2 Hz, 8H), 3.04 (d, J = 8.0 Hz, 2H), 2.62 (dd, J = 3.0, 1.8 Hz, 2H), 2.09 (d, J = 8.0 Hz, 1H), 1.55−1.47 (m, 2H), 1.43 (d, J = 8.8 Hz, 2H), 1.38−1.28 (m, 2H), 0.92 (d, J = 7.2 Hz, 3H). The ^{13}C NMR spectrum of compound **1** is shown in Figure S2. ^{13}C NMR (CD_3CN, 298 K, 100 MHz) δ (ppm): 173.4, 173.3, 148.4, 148.3, 137.9, 128.7, 121.1, 113.2, 112.5, 70.8, 70.7, 70.6, 70.4, 69.4, 68.3, 66. 2, 64.3, 47.1, 47.0, 45.6, 45.5, 44.9, 30.4, 18.9, 13.2. HRESIMS is shown in Figure S3: *m/z* calcd for $C_{32}H_{46}O_{11}$, 629.2938 $[M + Na]^+$; found 629.2925.

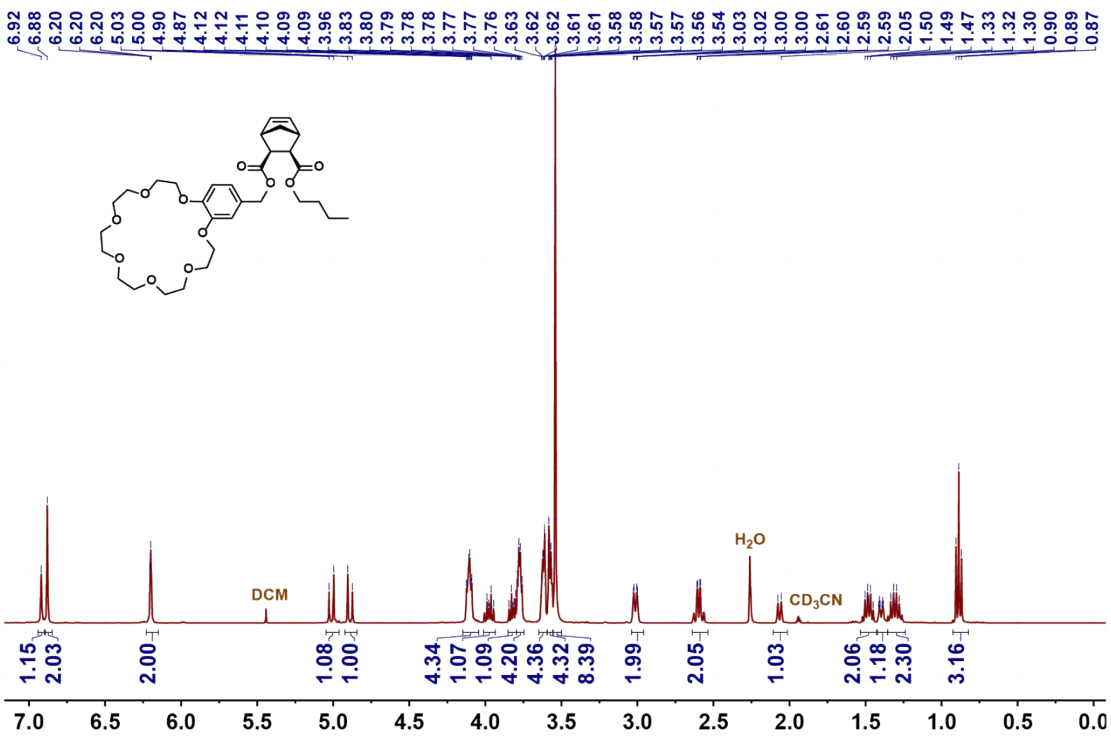


Figure S1. ^{1}H NMR spectrum (CD_3CN, 298 K, 400 MHz) of compound **1**.

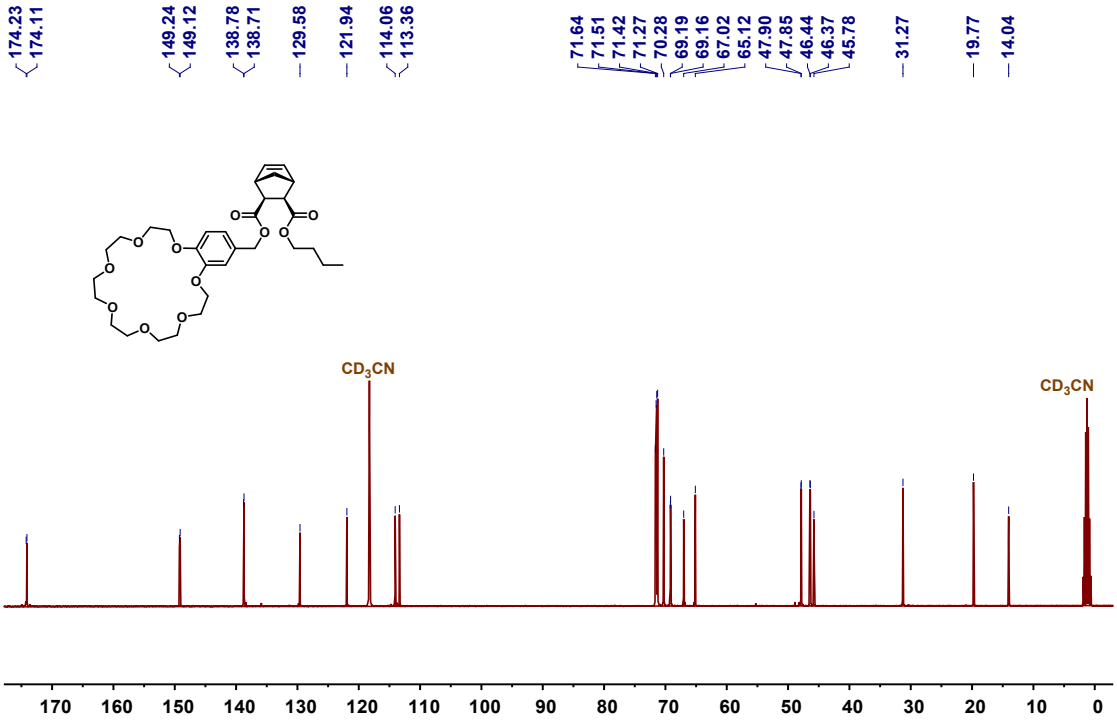


Figure S2. ^{13}C NMR spectrum (CD_3CN, 298 K, 100 MHz) of compound **1**.

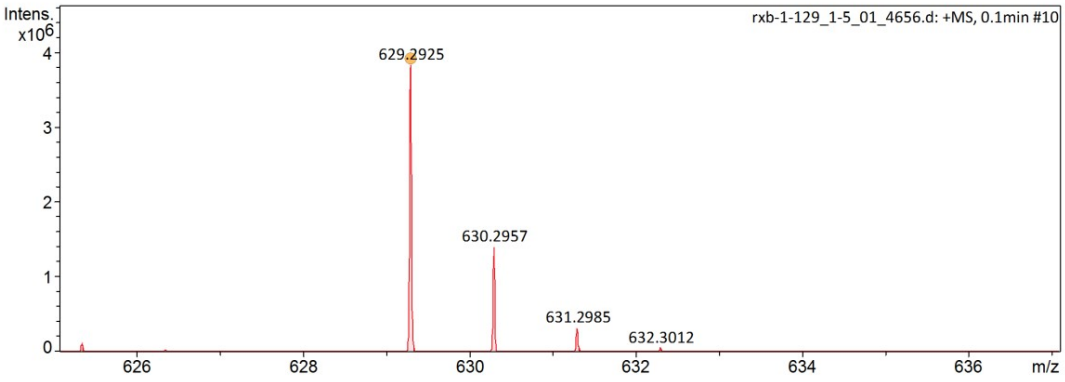
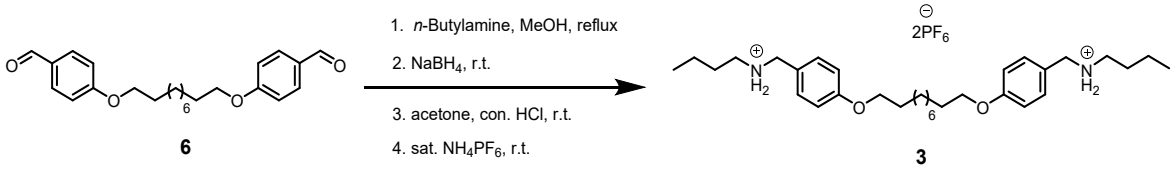


Figure S3. Electrospray ionization mass spectrum of compound **1**.

Synthesis of compound 3



Compound **6** (5.30 g, 13.9 mmol) and *n*-butylamine (2.24 g, 30.6 mmol) was heated to 70 °C in MeOH (60 mL) for 12 h. The reaction mixture was cooled to room temperature, $NaBH_4$ (1.58 g, 41.7 mmol) was added, and the mixture was stirred at room temperature for 12 h. The reaction was quenched by adding water dropwise. The aqueous layer was extracted with DCM twice and the combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was evaporated to dryness. The obtained oil was dissolved in acetone, then con. HCl solution was added. After stirred for 30 min, saturated NH_4PF_6 solution was added and stirred for 4 h. The product was extracted by DCM for 3 times, combined organic layer was dried over Na_2SO_4 and filtered. The solution was evaporated and the residue was purified by column chromatography to afford compound **3** as a white solid (7.13 g, 65%). M.p.= 57 °C. The ^{1}H NMR spectrum of compound **3** is shown in Figure S4. ^{1}H NMR (CD_3CN, 298 K, 400 MHz) δ (ppm): 7.39 (d, J = 8.6 Hz, 4H), 6.99 (d, J = 8.6 Hz, 4H), 4.11 (s, 4H), 4.02 (t, J = 6.8 Hz, 4H), 3.02 (t, J = 7.6 Hz, 4H), 1.82−1.74 (m, 4H), 1.69−1.60 (m, 4H), 1.52−1.34 (m, 16H), 0.95 (t, J = 7.4 Hz, 6H). The ^{13}C NMR spectrum of compound **3** is shown in Figure S5. ^{13}C NMR (CD_3CN, 298 K, 100 MHz) δ (ppm): 160.2, 131.7, 122.3, 114.8, 68.0, 51.1, 47.4, 29.3, 29.1, 28.9, 27.5, 25.7, 29.3, 12.7. HRESIMS is shown in Figure S6: *m/z* calcd for $C_{32}H_{54}N_2O_2$ charged 2+, 249.2087 $[M - 2PF_6]^{2+}$; found 249.2088.

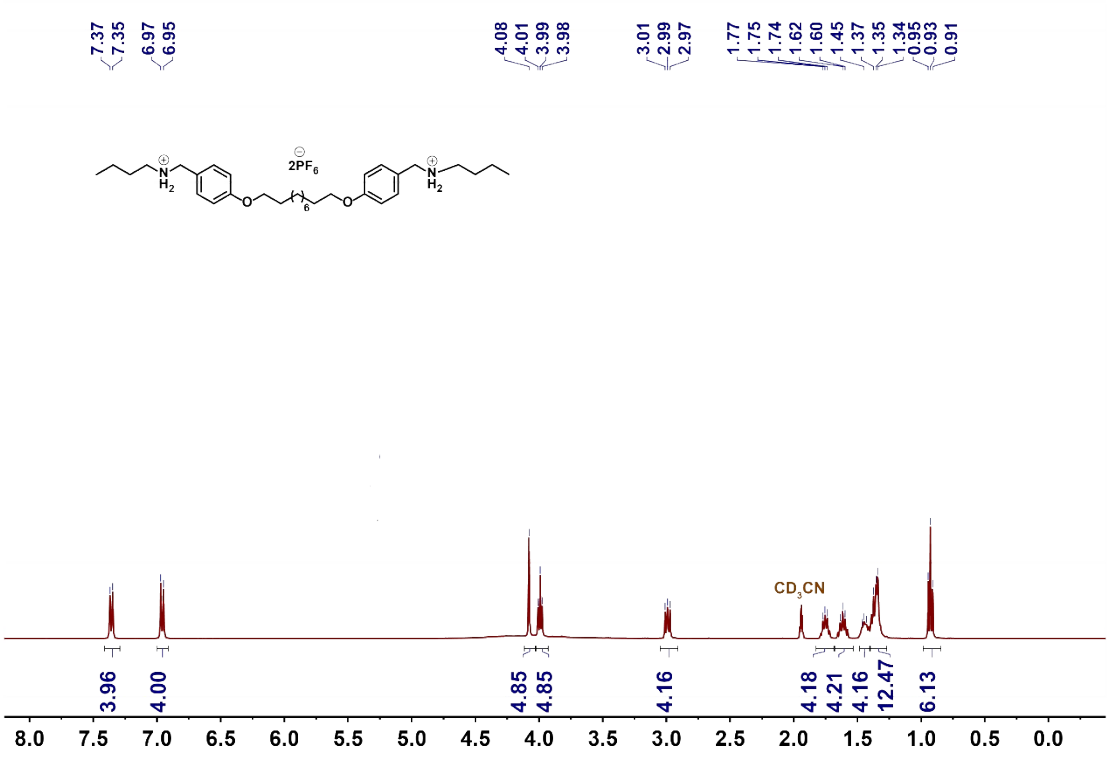


Figure S4. ^{1}H NMR spectrum (CD_3CN, 298 K, 400 MHz) of compound **3**.

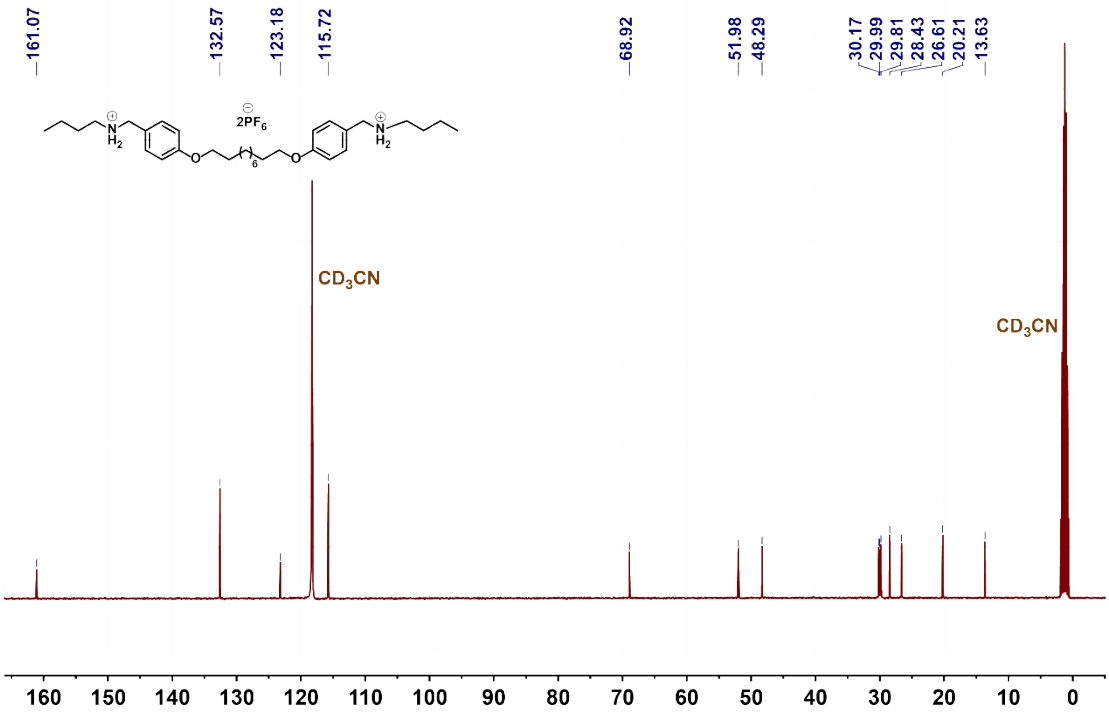


Figure S5. ^{13}C NMR spectrum (CD_3CN, 298 K, 100 MHz) of compound **3**.

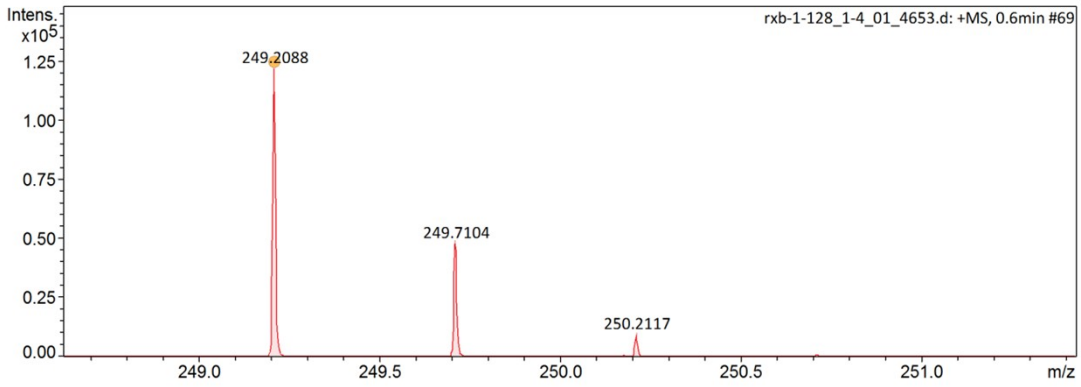
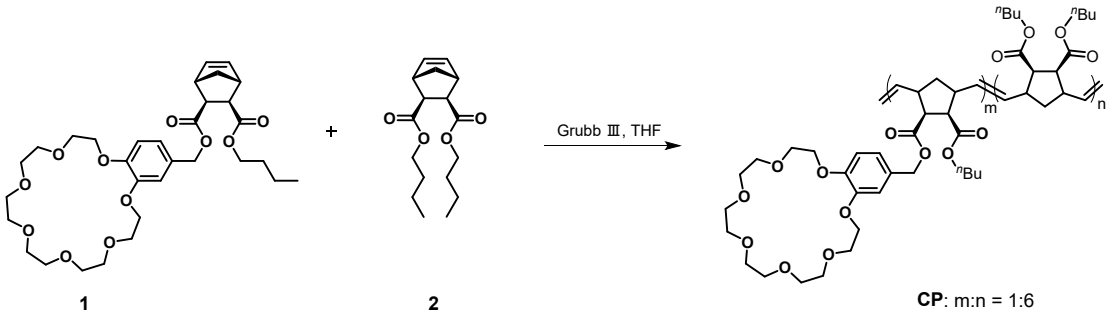


Figure S6. Electrospray ionization mass spectrum of compound **3**.

Synthesis of CP



An oven-dried vial was charged with monomer **1** (1.00 g, 1.65 mmol), monomer **2** (2.90 g, 9.89 mmol) and a stir bar. The vial was then degassed, and the 55 mL of degassed anhydrous THF was added via syringe under a nitrogen atmosphere to dissolve the monomers. The Grubbs III catalyst (23.8 mg, 0.028 mmol) in 4.0 mL of degassed anhydrous THF was injected into the monomer solution to initiate the polymerization. The solution was stirred for 16 h at room temperature and then quenched by the addition of 0.50 mL of neat ethyl vinyl ether. After stirring for an additional 60 min, the mixture was added dropwise to 600 mL of rapidly stirred MeOH and a white precipitate formed immediately. The suspension was then centrifuged and collected. The solid was dried under vacuum for 24 h to afford CP (3.51 g, 90%). The ^{1}H NMR spectrum of CP is shown in Figure S7. ^{1}H NMR (CD_3CN, 298 K, 400 MHz) δ (ppm): 6.97−6.86 (m, 3H), 5.46 (s, 6H), 5.35−5.19 (m, 7H), 5.01−4.91 (m, 2H), 4.14 (s, 4H), 4.08−3.89 (m, 24H), 3.81 (s, 4H), 3.68−3.62 (m, 4H), 3.62−3.59 (m, 4H), 3.58 (s, 8H), 3.31 (s, 8H), 2.98−2.77 (m, 18H), 2.21 (s, 20H), 1.65−1.49 (m, 22H), 1.43−1.29 (m, 26H), 1.01−0.89 (m, 36H). The SEC curve of CP is shown in Fig. S8 with M_n = 29631 g/mol and $Đ$ = 2.16.

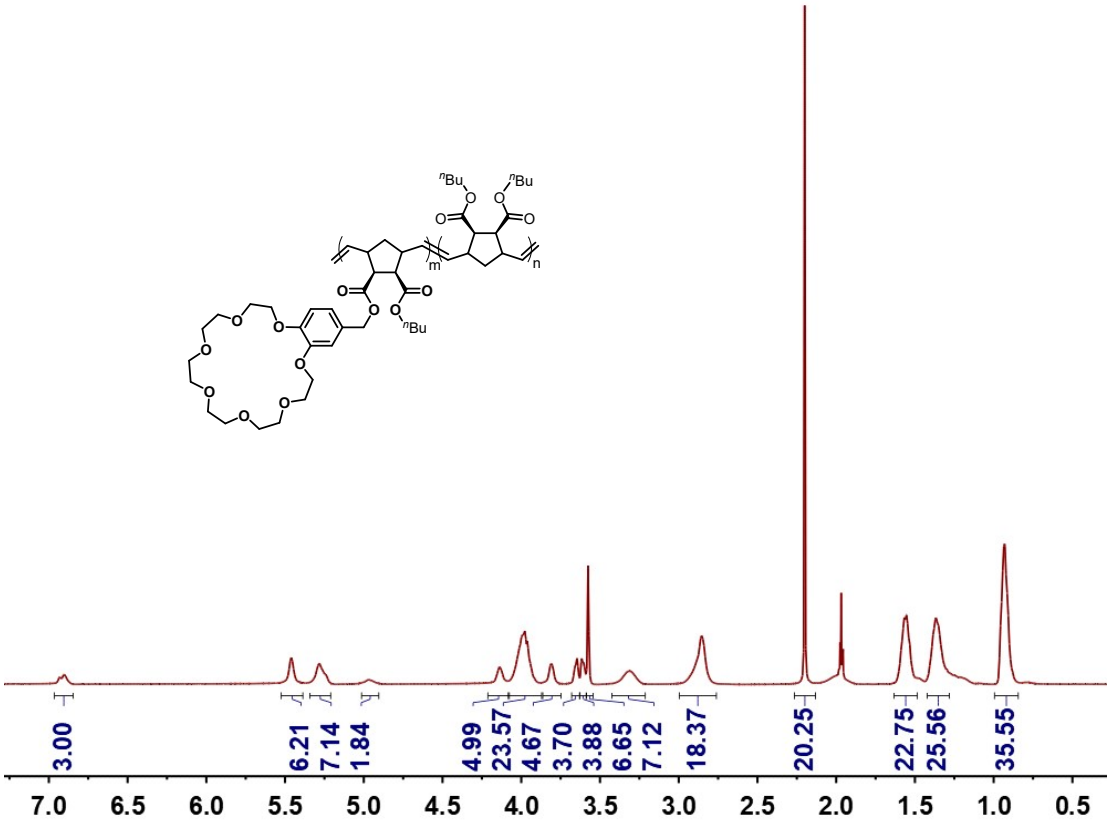


Figure S7. ^{1}H NMR spectrum (CD_3CN, 298 K, 400 MHz) of CP.

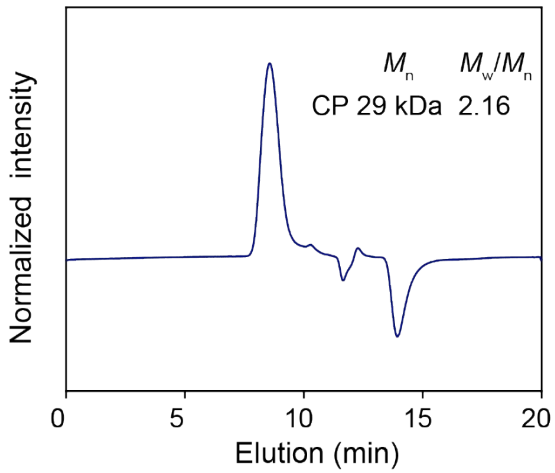


Figure S8. GPC elution curve of CP with DMF as the eluent and polystyrene (PS) as the standard.

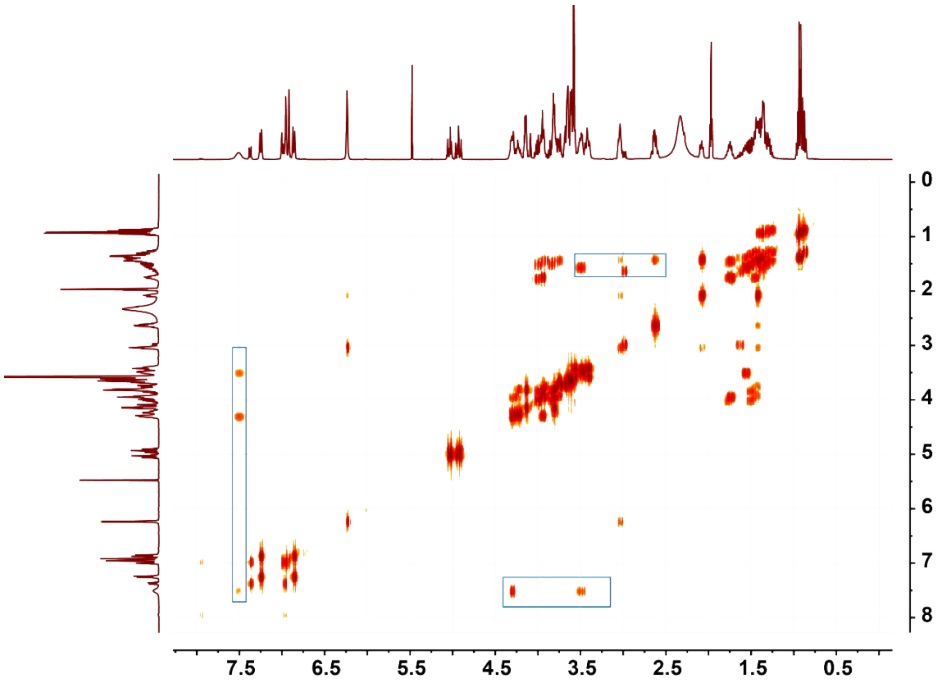


Figure S9. COSY NMR spectrum (400 MHz, 298 K, CD_3CN) of the mixture of monomer **1** and cross-linker (the molar ratio of model monomer to cross-linker is 2:1).

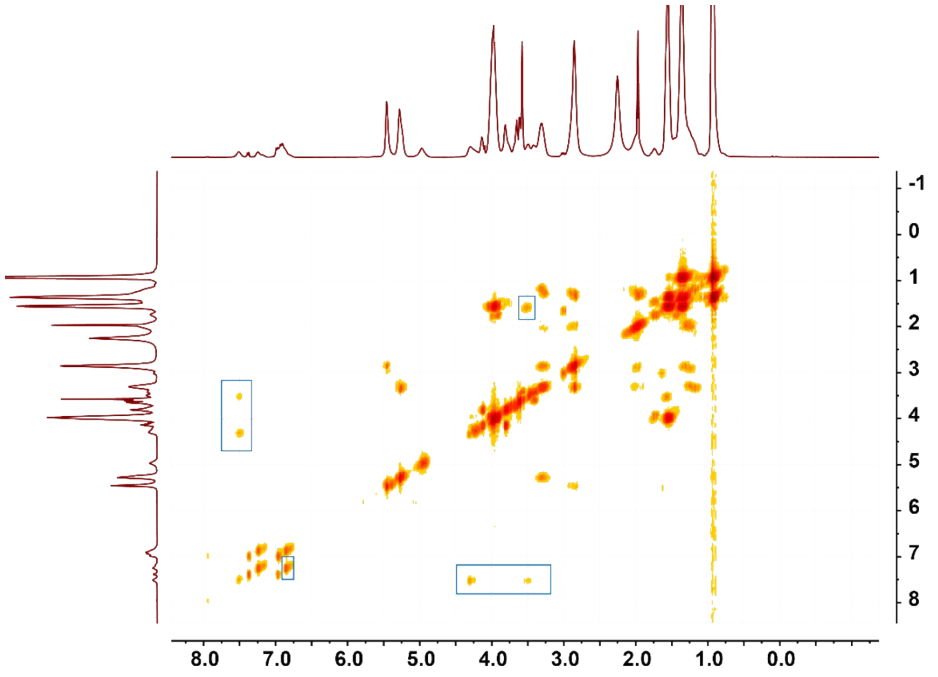


Figure S10. COSY NMR spectrum (400 MHz, 298 K, CD_3CN) of SPN-**5**.

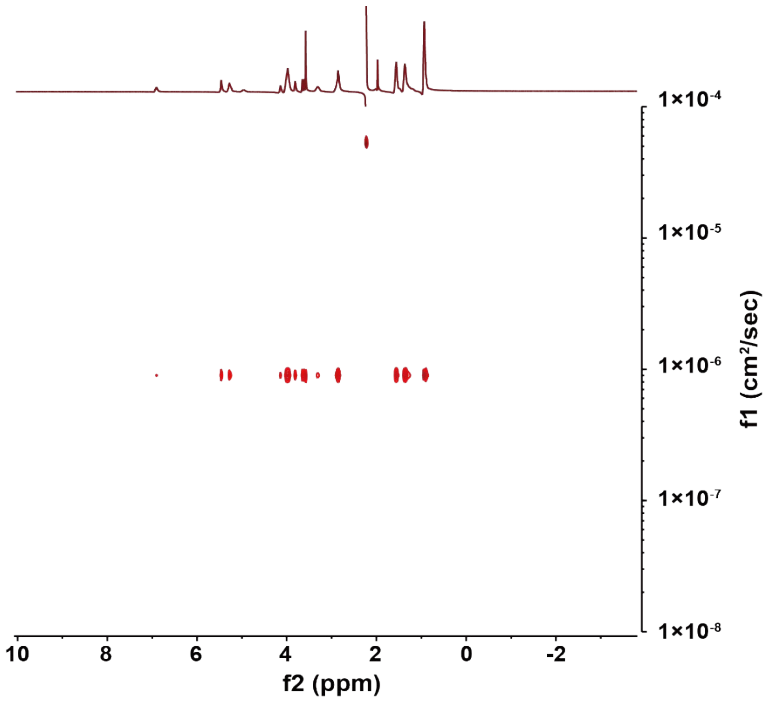


Figure S11. DOSY NMR spectrum (400 MHz, 298 K, CD_3CN) of CP.

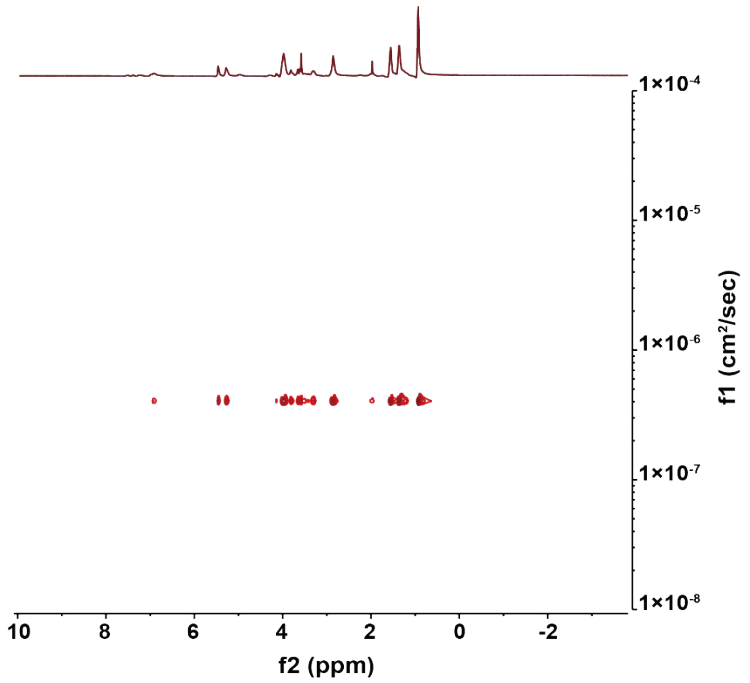


Figure S12. DOSY NMR spectrum (400 MHz, 298 K, CD_3CN) of SPN-**5**.

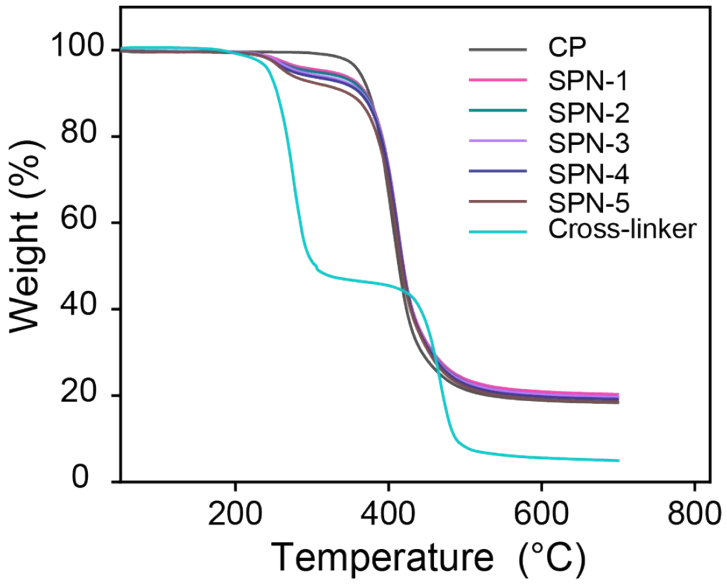


Figure S13. TGA curves of CP, SPNs-**1**−**5** and cross-linker recorded under N_2 flow (50 mL/min) with a heating rate of 20 °C/min.

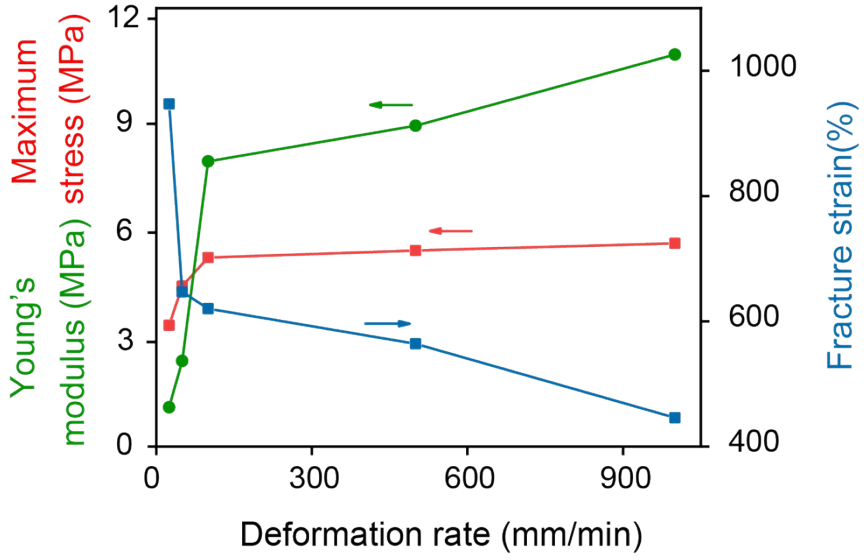


Figure S14. Deformation rate dependence of SPN-**5** on maximum stress, Young's modulus and fracture strain calculated from their stress–strain curves in Fig 2d.

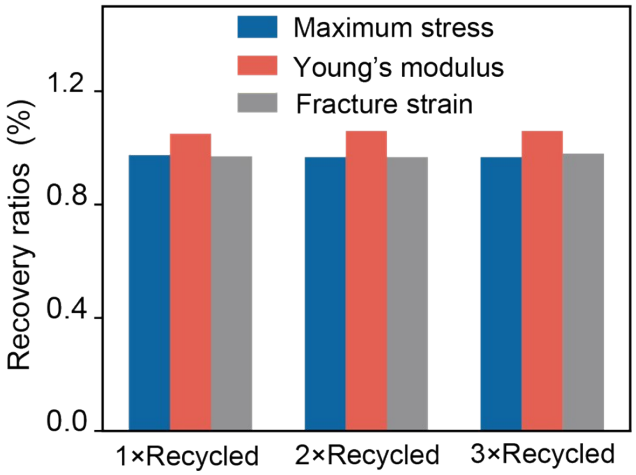


Figure S15. Recovery ratio of mechanical performance for recycled SPN-**5** calculated from their stress–strain curves in Fig 4d.

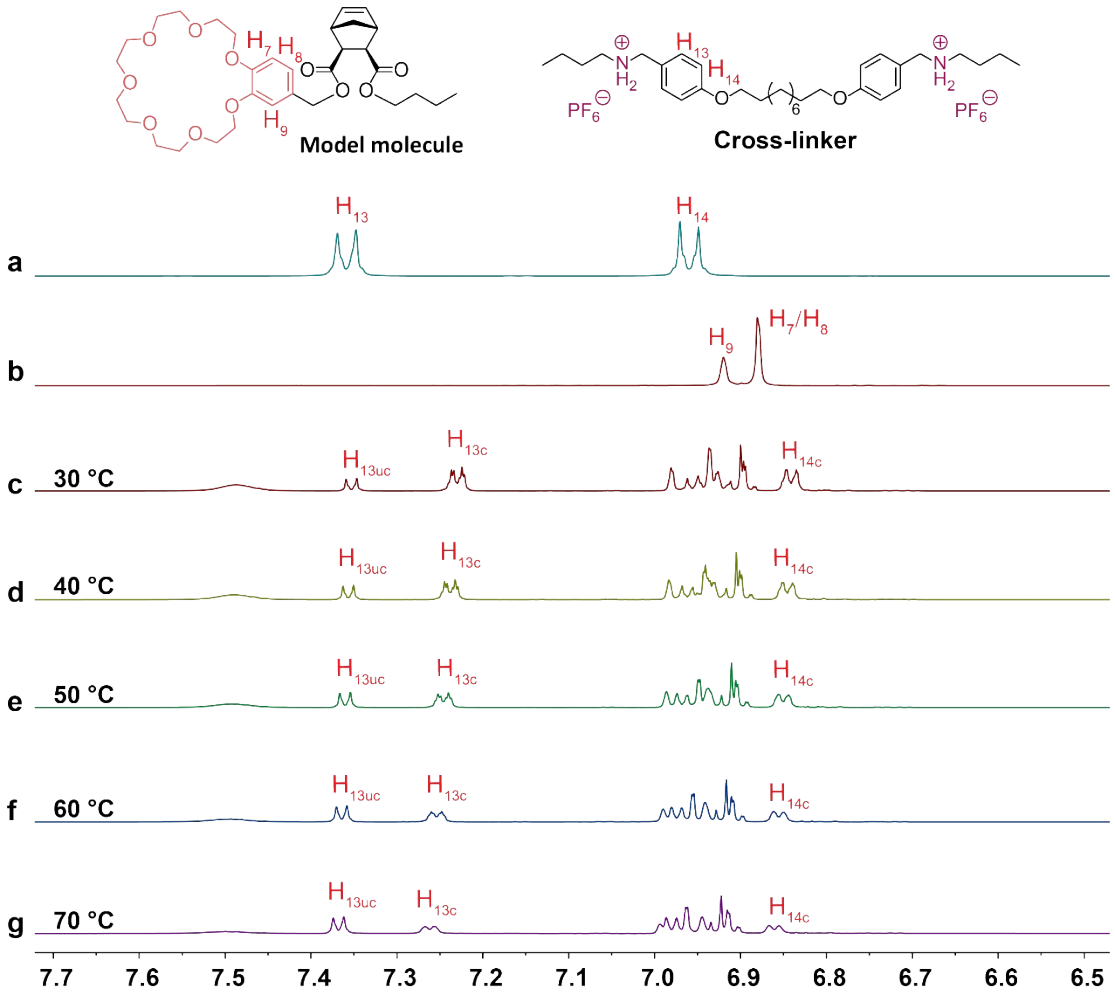


Figure S16. Partial varied-temperature ^{1}H NMR spectra (700 MHz, CD_3CN) of (a) cross-linker, (b) model monomer (B21C7 functionalized norbornene), and the mixture of model monomer and cross-linker (the molar ratio of monomer to cross-linker is 2:1): (c) 30 °C, (d) 40 °C, (e) 50 °C, (f) 60 °C, and (g) 70 °C. Here "c" and "uc" denote complexed and uncomplexed species, respectively.

References:

S1. L. M. Rice and E. E. Reid, *J. Am. Chem. Soc.*, 1952, **74**, 3955−3956.

S2. Z. M. Zhang, L. Cheng, J. Zhao, L. Wang, K. Liu, W. Yu and X. Z. Yan, *Angew. Chem. Int. Ed*., 2020, **59**, 12139–12146.

S3. A. M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *J. Am. Chem. Soc.*, 2005, **127**, 12612–12619.