Supporting Information

Bio-complementary Supramolecular Polymers with Effective Self-Healing Functionality

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Experimental section:

Materials

N-Phenylaminopropyl POSS® cage mixture (n= 8, 10, 12) was purchased from Hybrid Plastics (Hattiesburg, MS, USA). All other chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA) in the highest purity available and were used without further purification. All solvents were high-performance liquid chromatography (HPLC) grade and obtained from TEDIA (Fairfield, OH, USA). Tetrahydrofuran (THF) and dimethylformamide (DMF) were distilled over calcium hydride prior to use.

Measurements

Nuclear Magnetic Resonance (NMR). ^{1}H NMR spectra were recorded using a Varian Inovain 400

MHz spectrometer (Palo Alto, CA, USA). All samples of ca. 15 mg were dissolved in approximately 0.6 ml of deuterated solvent and analyzed at 25°C.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were measured using a Nicolet Avatar 320 FTIR Spectrometer (Madison, WI, USA); 32 scans were collected at a resolution of 1.0 cm^{-1}. The sample chamber was purged with nitrogen in order to maintain film dryness.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy (MALDI-TOF MS). MALDI-TOF MS was performed using a Bruker Autoflex II instrument (Billerica, MA, USA) equipped with a nitrogen laser (337 nm, 3 ns pulse, over 20 Hz maximum firing rate).

Gel permeation chromatography (GPC). The weight-average molecular weight (*Mw*), number-average molecular weight (*Mn*), and polydispersity index (PDI; *Mw/Mn*) were measured using a Waters 410 GPC system equipped with a refractive index detector and three Ultrastyragel™ columns (100, 500 and 1000 Å) connected in series. Dimethylformamide (DMF) was used as the eluent at a flow rate of 1.0 ml/min at 40°C. The system was calibrated using polystyrene (PS) standards (Polymer Standards Service, MD, USA).

Differential Scanning Calorimetry (DSC). A DSC instrument (TA Instruments Q-20, New Castle, DE, USA) was used to perform thermal analysis. Test samples (ca. 4–6 mg) were weighed and sealed in an aluminum sample pan. The temperature range -50 to 140°C was scanned at 10 °C/min.

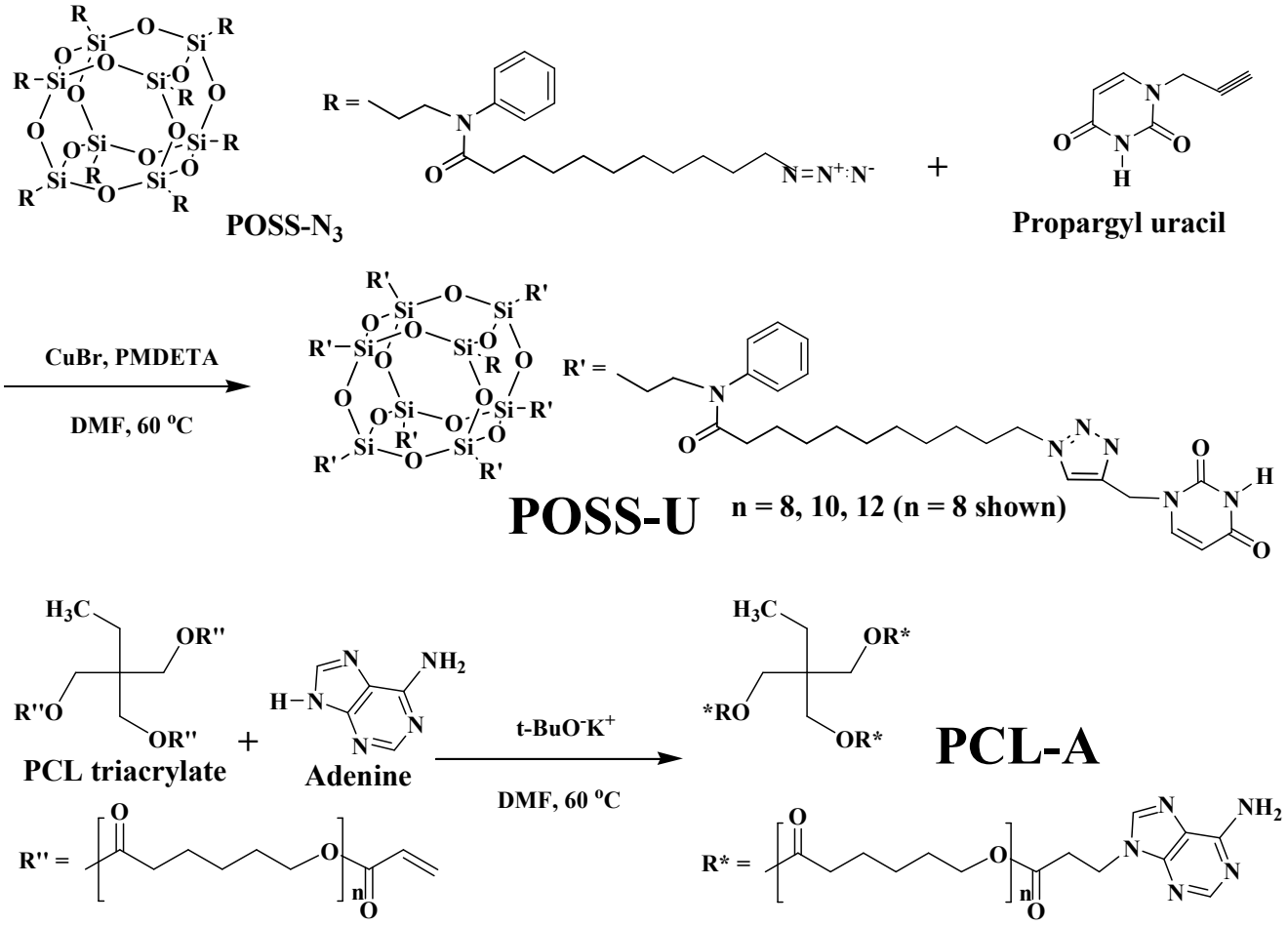
Tensile tests. Tensile tests were performed using a universal tester (EZ-L; Shimadzu Corp, Kyoto, Japan) at a constant cross-head speed of 10 mm/min. All tests were performed under ambient conditions (20°C, 65% relative humidity). Healing efficiency was estimated as the ratio of the fracture toughness of the self-healed samples and original samples.

Synchrotron Wide-angle X-ray Diffraction (WAXD). XRD measurements were performed using a BL17A1 wiggler beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Radiation with a wavelength of 0.1330898 nm was used. The beam size at the sample position was set to ca. 20.0 mm in diameter, as defined by a pinhole collimator.

Viscosity measurements. The dynamic viscosity experiments were performed using a Physical MCR501 rheometer (Anton Paar Ltd, St. Albans, UK) with cone/plate measuring geometry. All tests were carried out under a nitrogen atmosphere. Variable-temperature control was applied to obtain dynamic viscosity. The gap distance was set to 0.055 mm. Samples were scanned from 40 to 120°C at a rate of 3.0°C/min, and the shear rate and frequency were fixed to 10 s^{-1} and 1 Hz, respectively.

Scanning Electron Microscopy (SEM). The healed films were firmly fixed onto the silicon substrate before SEM scanning, sputtered with platinum and measured using a field-emission scanning electron microscope (Hitachi S-4700, Tokyo, Japan) at an accelerating voltage of 15 kV.

Syntheses



Scheme S1. Synthetic procedures for POSS-U and PCL-A.

Synthesis of POSS-N_3

11-Azidoundecanoic acid was synthesized from commercial 11-bromoundecanoic acid according to previously described procedures.[S1] 11-Azidoundecanoic acid (9.83 g, 40.0 mmol) was first treated with an excess of thionyl chloride (11.6 ml, 160.0 mmol) and refluxed for 2 h, then 11-azidoundecanoyl chloride (9.52 g) was obtained by evaporating the thionyl chloride and dried under vacuum. *N*-Phenylaminopropyl POSS (5 g, 3.4 mmol) and triethylamine (5.1 g, 50.2 mmol) were dissolved in dry THF (200 ml) cooled to 0°C in an ice bath. A solution of 11-azidoundecanoyl chloride in dry THF (50 ml) was added drop-wise via a syringe over a period of 1.5 h, then the reaction mixture was stirred at 0°C for 3 h and maintained at room temperature for an additional 16 h. After evaporating the solvent,

the residue was subjected to flash column chromatography (silica gel, 70% *n*-hexane/ethyl acetate) to obtain the product. Finally, the solvent was evaporated, and the viscous liquid product was dried under vacuum, yield: 8.7 g (81%). ^{1}HNMR ($CDCl_3$, 400 MHz), δ (n = 10): 7.39 (20H, br), 7.30 (10H, br), 7.09 (20H, br), 3.54 (20H, br), 3.24 (20H, br), 1.96 (20H, br), 1.56 (20H, br), 1.24 (140H, br), 1.13 (20H, br), 0.28 (20H, br) ppm.

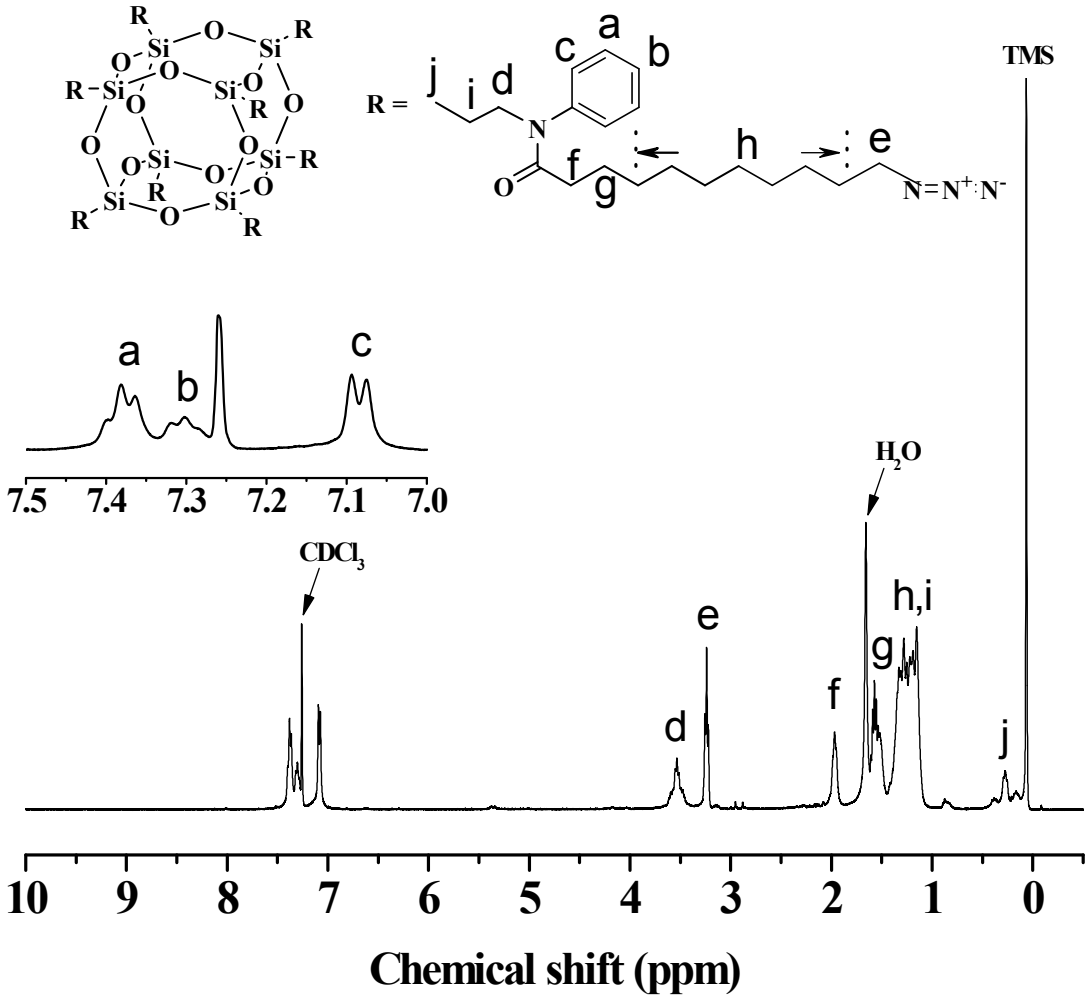


Fig. S1: ^{1}H-NMR spectrum of POSS-N_3 in $CDCl_3$.

Synthesis of POSS-U

Propargyl uracil was synthesized from uracil and propargyl chloride as previously described.[S2] Propargyl uracil (5 g, 33.11 mmol) and POSS-N_3 (7 g, 2.06 mmol) were dissolved in DMF (100 ml) and

then the resulting solution was purged with dry argon for 0.5 h. N,N′,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA; 35.3 µL, 0.014 mmol) and copper bromide CuBr (0.15g) were added to the flask, resulting in a light green solution. The solution was heated to 60°C and stirred under an argon atmosphere until the azide peak (2095 cm^{-1}) completely disappeared as observed via FTIR spectroscopy. After cooling to room temperature, the reaction mixture was passed through a neutral aluminum oxide column to remove the copper catalyst. Finally, the DMF was distilled off using a vacuum evaporator and the product was washed several times in methanol. The light brown powder POSS-U was collected by vacuum drying. Yield: 8.2 g (87%). ^{1}HNMR (DMSO-d_6, 400 MHz), δ (n = 10): 11.28 (10H, br), 8.02 (10H, br), 7.71 (10H, br), 7.37 (20H, br), 7.24 (10H, br), 7.14 (20H, br), 5.54 (10H, br), 4.89 (20H, br), 4.23 (20H, br), 2.96 (20H, br), 1.85 (20H, br), 1.71 (20H, br), 1.34 (20H, br), 1.06 (120H, br), 0.21 (20H, br) ppm.

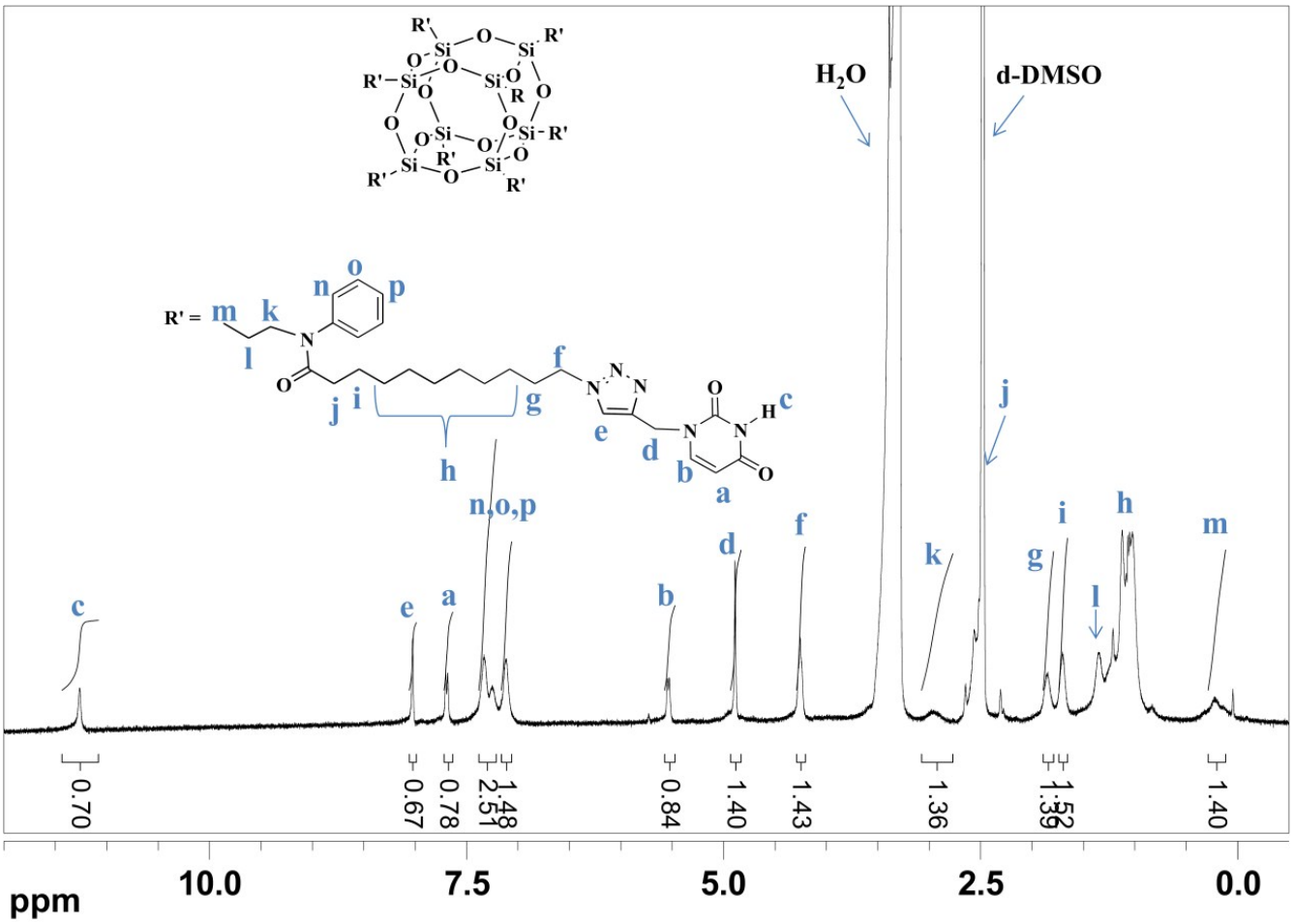


Fig. S2: ^{1}H-NMR spectrum of POSS-U in DMSO-*d*6

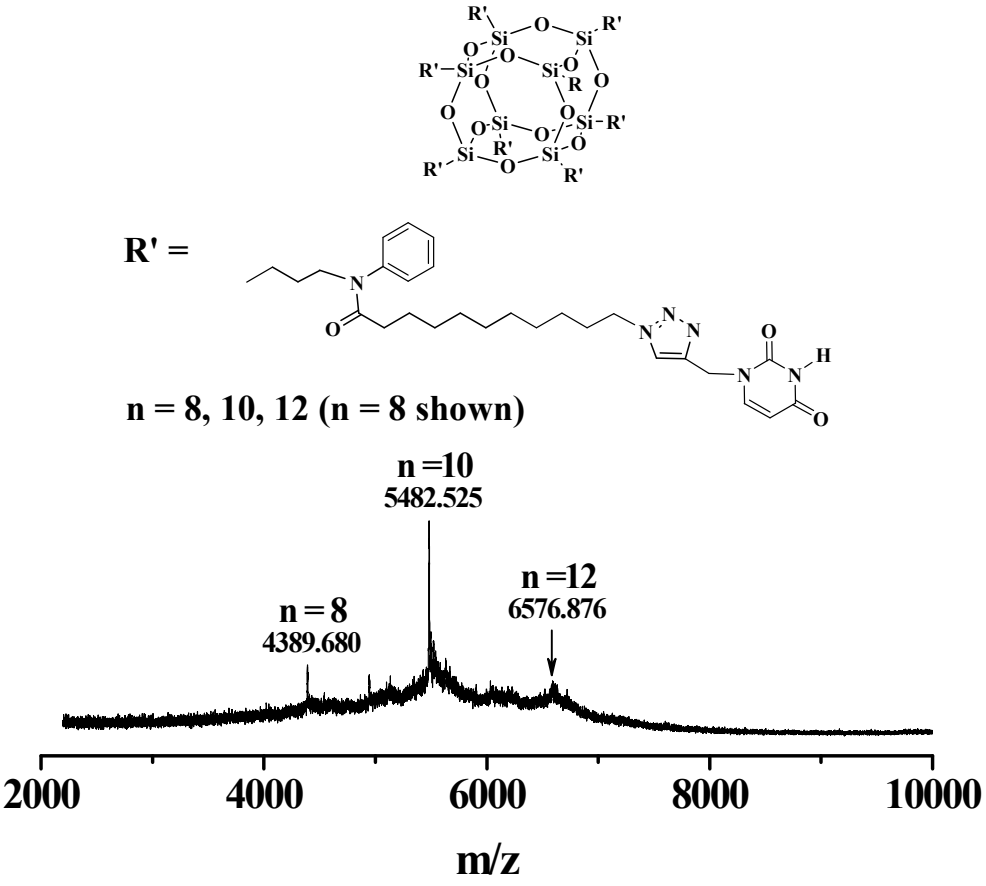


Fig. S3: MALDI-TOF mass spectrum of POSS-U.

Synthesis of PCL-A

PCL triacrylate was synthesized from the monomers PCL triol (M_w = 900) and acryloyl chloride as previously described.[S3] PCL triacrylate (10 g, 9.4 mmol), adenine (9 g, 59.2 mmol) and potassium tert-butoxide (0.34 g, 3.0 mol) were solved in 200 ml of DMF in a flask and the reaction mixture was stirred at 70°C for 2 d. After solvent evaporation, the crude product was re-dissolved in chloroform (250 ml) with vigorous stirring for 3 h and insoluble solids were removed by filtration. Finally, the chloroform was evaporated and the product was dried under a vacuum. Yield: 12.2g (86%). ^{1}HNMR ($CDCl_3$, 400 MHz), δ (n = 3): 8.33 (3H, br), 7.91 (3H, br), 5.99 (6H, br), 4.49 (6H, br), 4.05 (PCL segement, br), 3.99 (6H, br), 2.92 (6H, br), 2.29 (PCL segement, br), 1.63 (PCL segement, br), 1.36 (PCL segement, br), 1.30 (2H, br), 0.87 (3H, br) ppm.

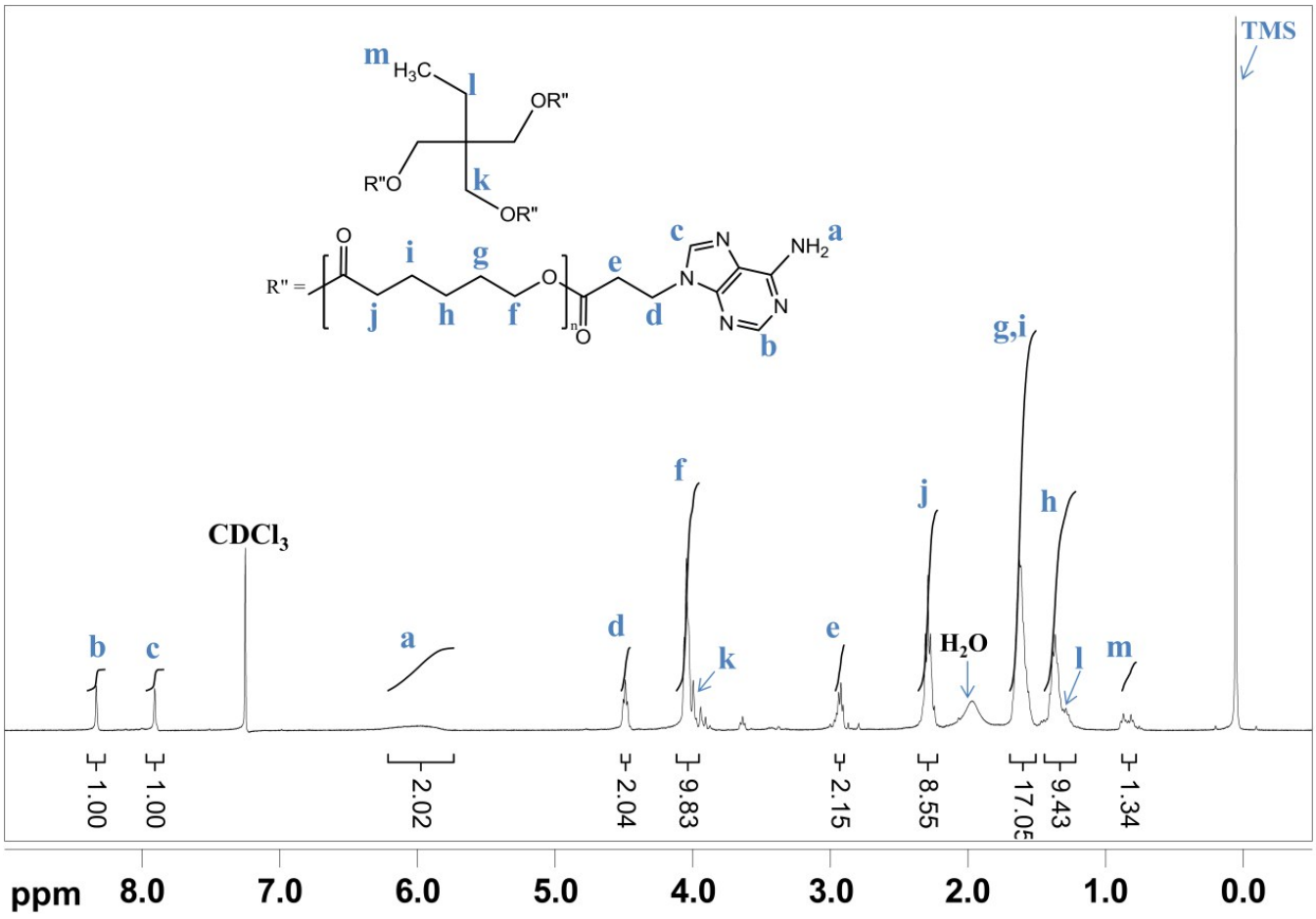


Fig. S4: ^{1}H-NMR spectrum of PCL-A in $CDCl_3$

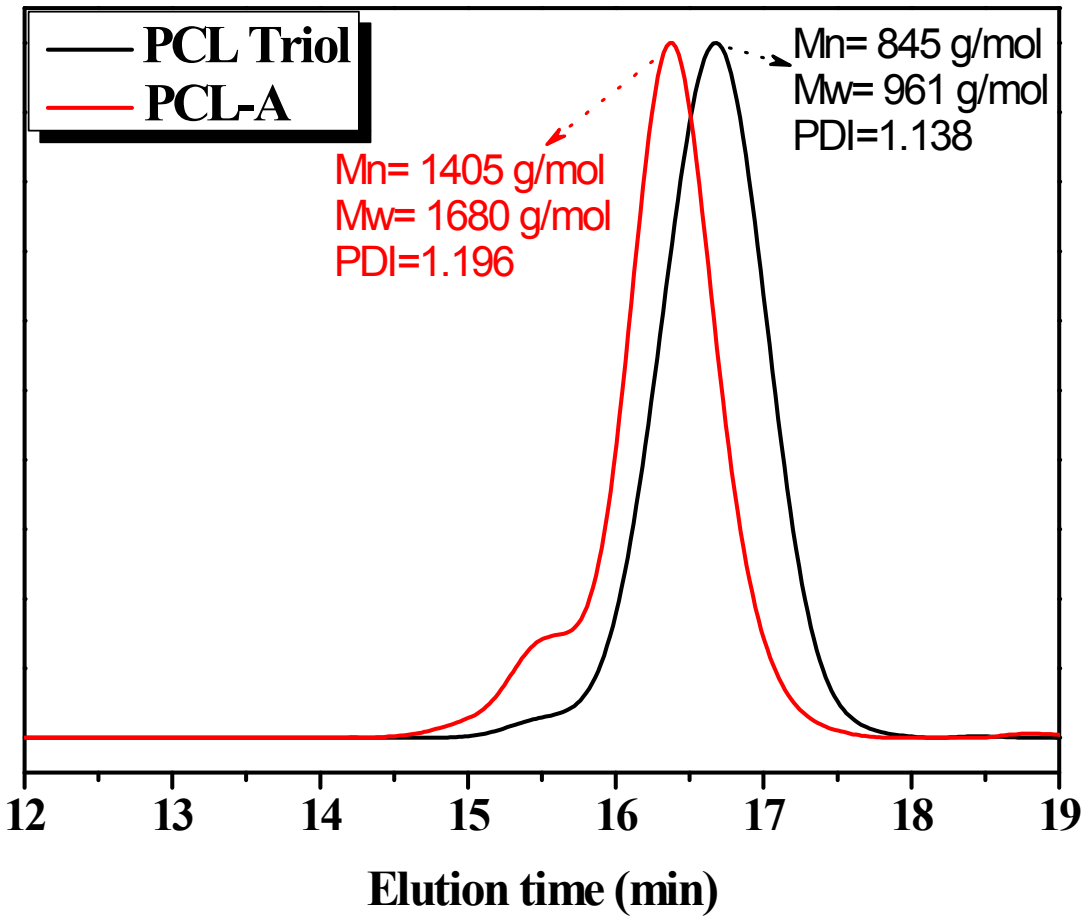


Fig. S5: GPC traces of PCL triol and PCL-A

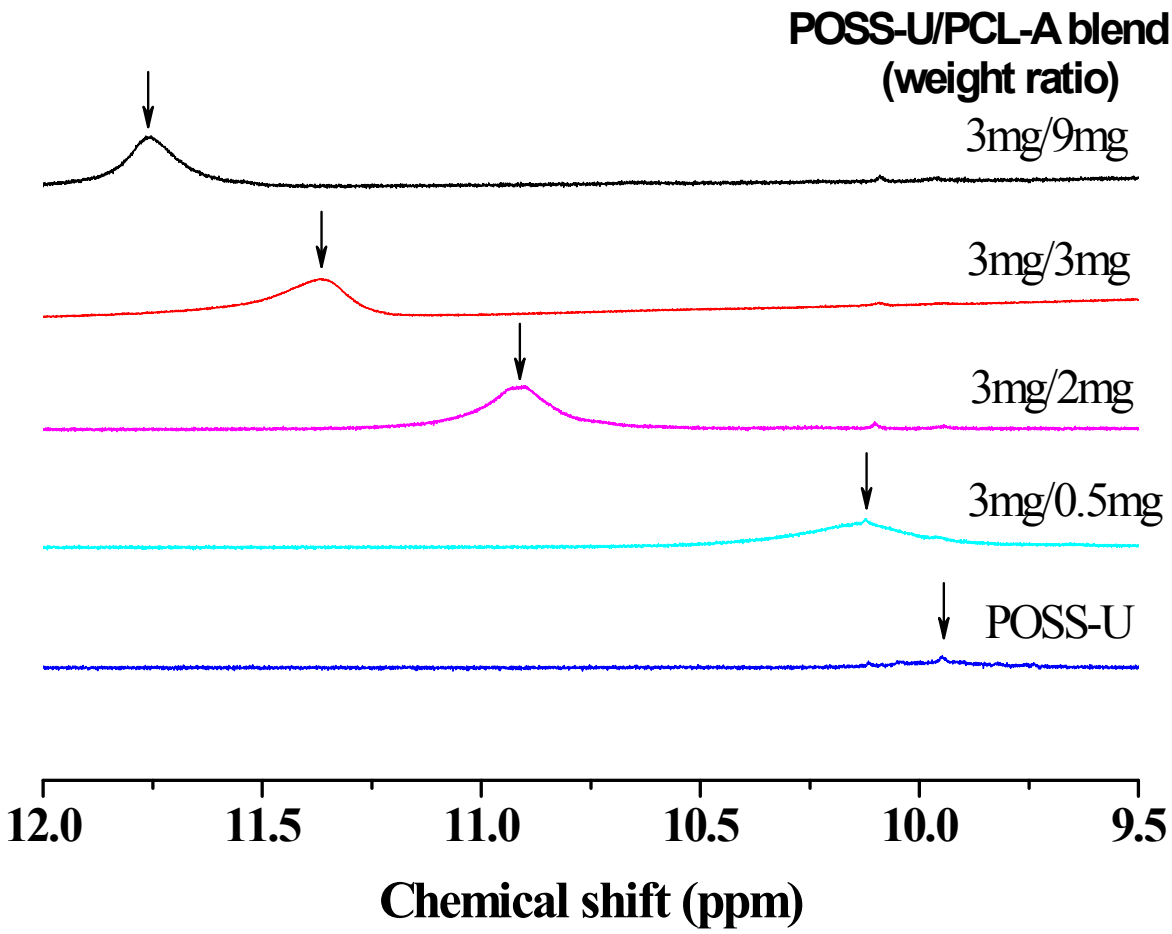


Fig. S6: 1H NMR spectra obtained from 1H NMR titration experiment of POSS-U/PCL-A complexes in tetrachloroethane-d_2 at 25 °C. The N-H region of the ^{1}H-NMR spectrum of POSS-U after the addition of PCL-A is indicated.

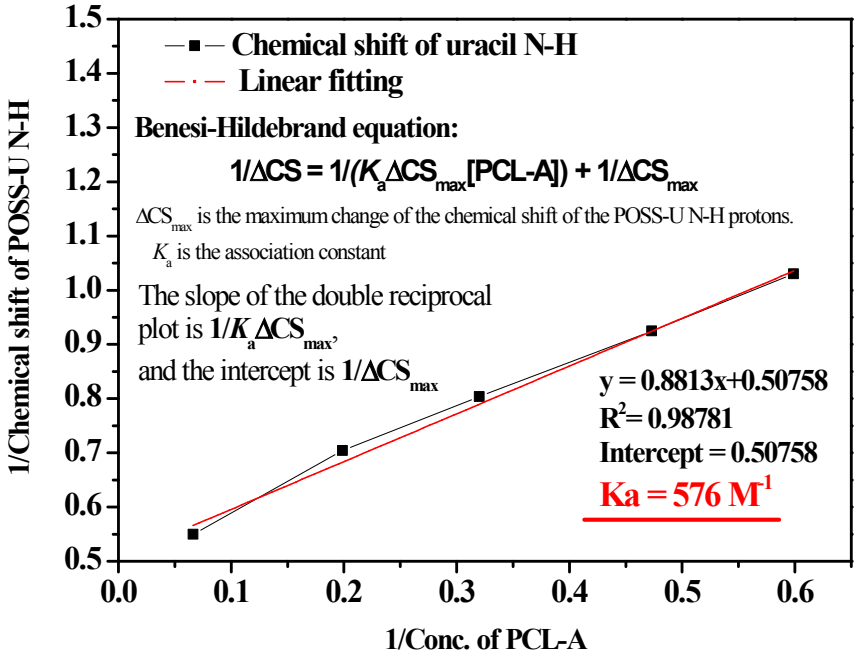


Fig. S7: Benesi–Hildebrand plots for the POSS-U/PCL-A association in tetrachloroethane-d_2 at 25°C.

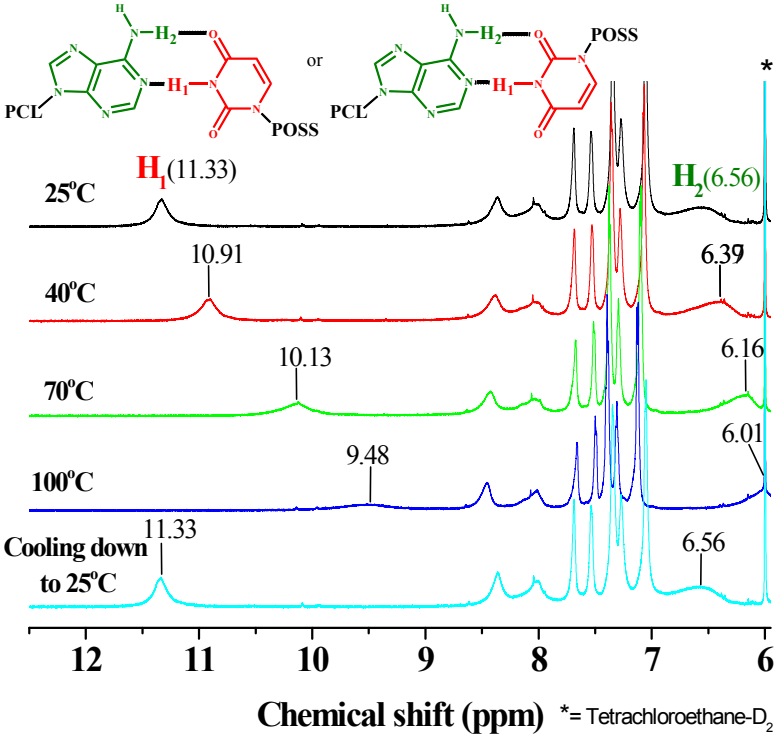


Fig. S8: 1H-NMR spectra for the 3/1 POSS-U/PCL-A complex in tetrachloroethane-d_2 at various temperatures. The sample was allowed to equilibrate for 20 min at each temperature.

$$Young's\ modulus = \frac{3\rho RT}{M_c}$$

Fig. S9: Relationship of the average molecular mass with crosslinks (M_c), Young's modulus and the density of the POSS-U/PCL-A blend (ρ). The 10/1, 3/1 and 1/1 POSS-U/PCL-A blends had viscosities of 1.26, 1.21 and 1.19 g/cm^3, respectively, at 25°C.

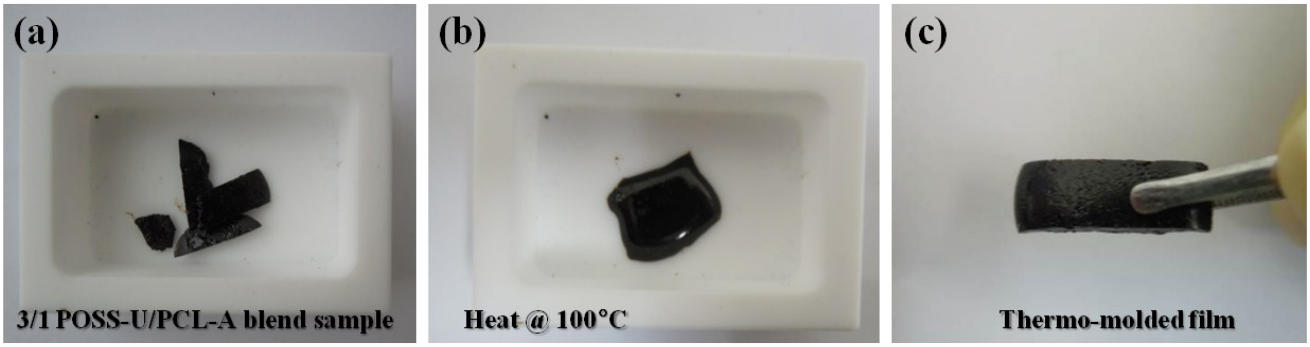


Fig. S10: Rapid film-forming reprocessing of self-assembled POSS-U/PCL-A composites. The chopped POSS-U/PCL-A film was placed in a Teflon mold (a) and reprocessed at 100°C for 20 minutes (b) to result in a film (c).

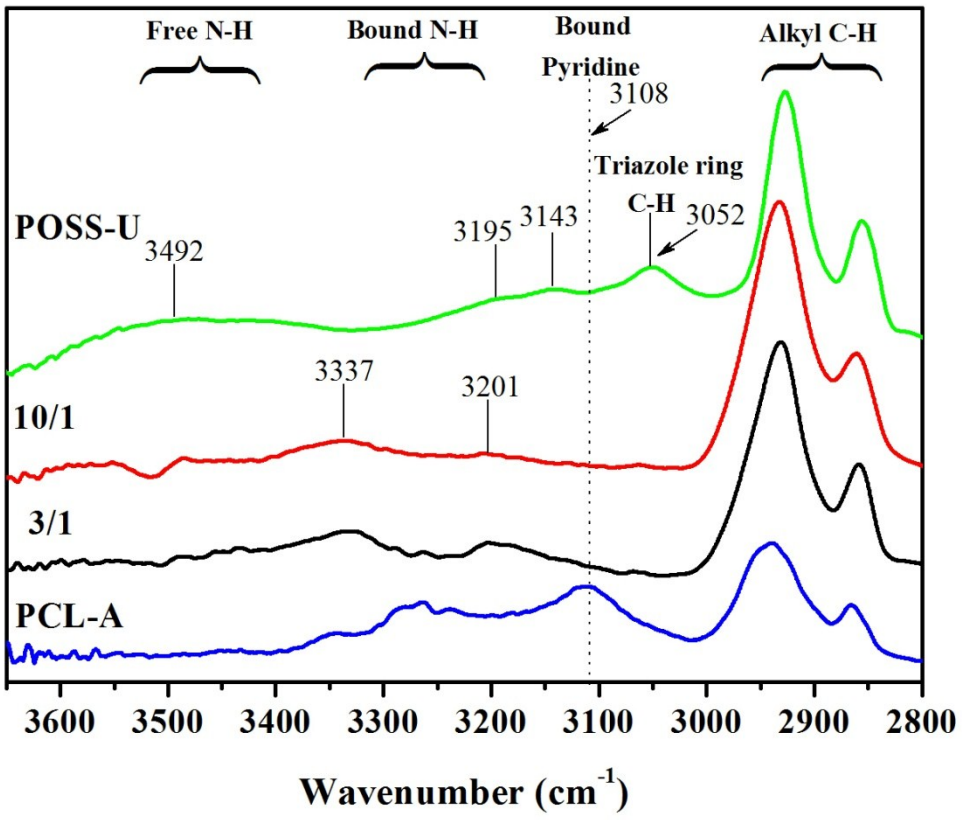
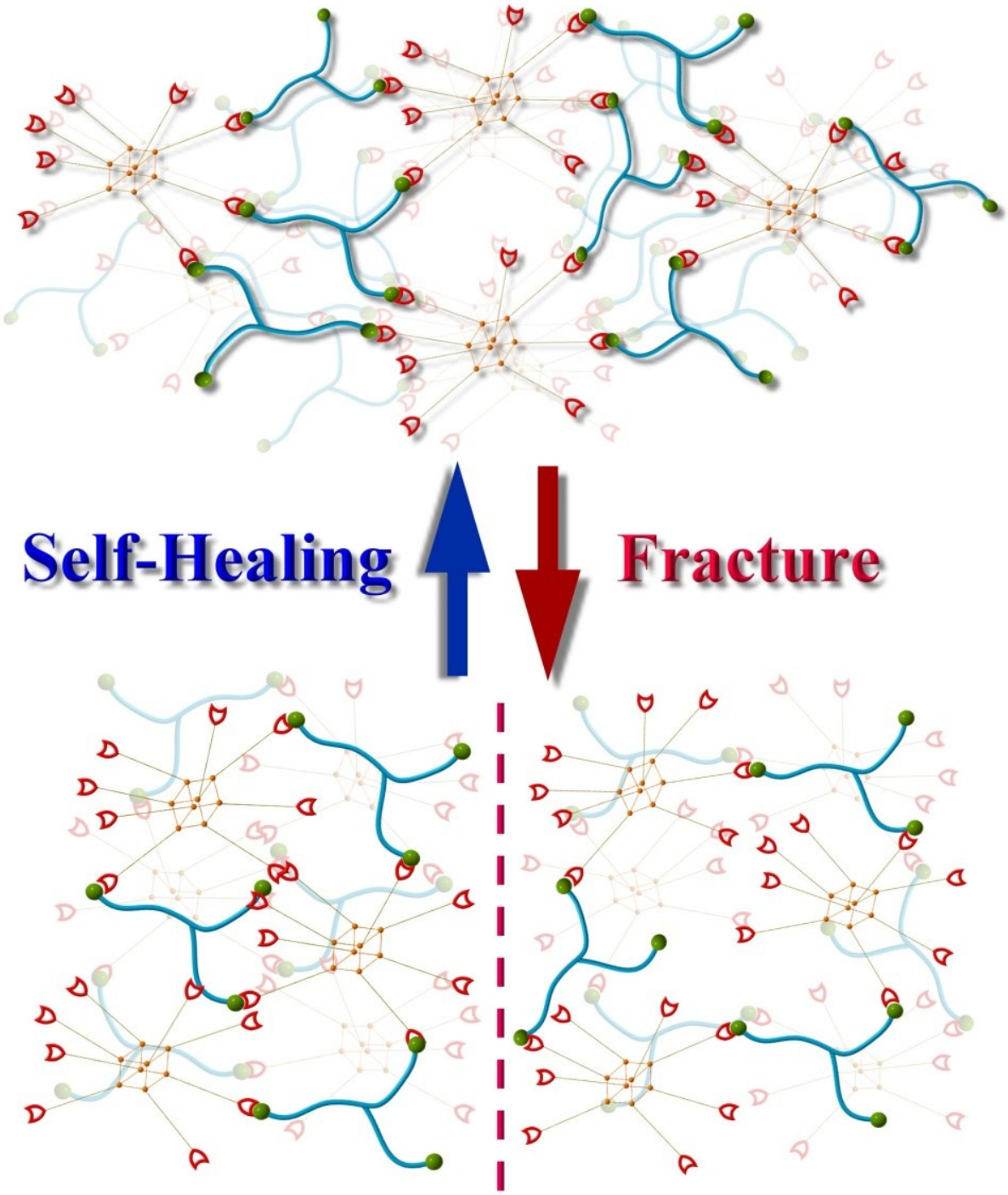


Fig. S11: FTIR spectra recorded at 25°C in the range 2700–3700 cm^{-1} for POSS-U in the bulk state in the presence of different molar ratios of PCL-A.

Figure S11 shows the FTIR (Fourier Transform Infrared Spectrometer) spectra in the N–H stretching absorption region of the POSS-U/PCL-A complexes. The characteristic peak at 3492 cm^{-1} can be attributed to the free amide N–H group of POSS-U and other peaks at 3143 cm^{-1} and 3195 cm^{-1} involved in uracil-uracil (U-U) interactions.[S4] The presence of the peak at 3492 cm^{-1} indicates that a fraction of the uracil side groups of POSS-U was not involved in U-U interactions.[S4] The peak of the free amide N–H stretching mode at 3492 cm^{-1} disappeared upon increasing the amount of added PCL-A, suggesting that POSS-U interacted strongly with PCL-A and that uracil–adenine (U-A) interactions were more favorable than their self-interactions (U–U and Adenine–Adenine). FT-IR spectra showed the presence of peaks at 3201 and 3337 cm^{-1} corresponded to hydrogen-bonded amide N–H groups at 10/1 and 3/1 POSS-U/PCL-A complexes, indicating that POSS and PCL-A formed a three-dimensional hydrogen-bonded network in the bulk state.



Scheme S2. Self-healing mechanism for a supramolecular polymer network formed by fracture-induced triggering of the complementary base pair uracil-adenine system.

References

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S2. J. Krim, B. Sillahi,1 M. Taourirte, E. M. Rakib, J. W. Engels, *Arkivoc*, 2009, **xiii**, 142–152.

S3. H. M. Kim, H. R. Kim, C. T. Hou and B. S. Kim, *J. Am. Oil. Chem. Soc.*, 2010, **87**, 1451–1459.

S4. C. C. Cheng, Y. C. Yen, Y. S. Ye and F. C. Chang, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 6388–6395.