

Supplementary Information for:

**Multi-Stimuli-Responsive Self-Healing Metallo-Supramolecular
Polymer Nanocomposites**

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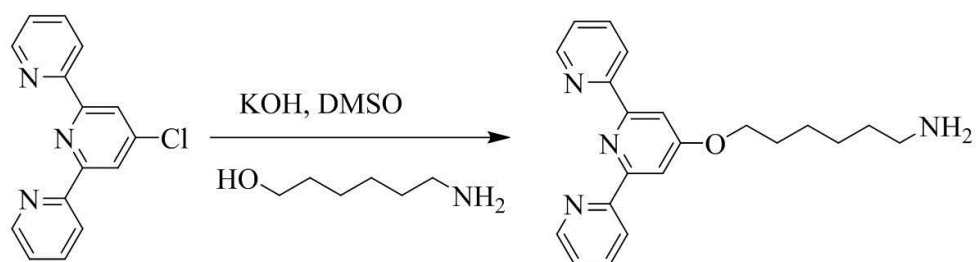
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Movie S1. Shape memory test.

Synthesis of 6-(2, 2':6', 2''-Terpyridin-4'-yloxy)-hexan-1-amine (tpy-NH₂)



¹H NMR (300 MHz, DMSO-*d*₆, δ): 8.68 (d, 2H, Ar-H), 8.60 (d, 2H, Ar-H), 8.00 (d, 2H, Ar-H), 7.94 (s, 2H, Ar-H), 7.48 (dd, 2H, Ar-H), 4.23 (t, 2H, -OCH₂), 3.38 (t, 2H, -CH₂N-), 1.23-1.84 (m, 8H, -CH₂-) ppm.

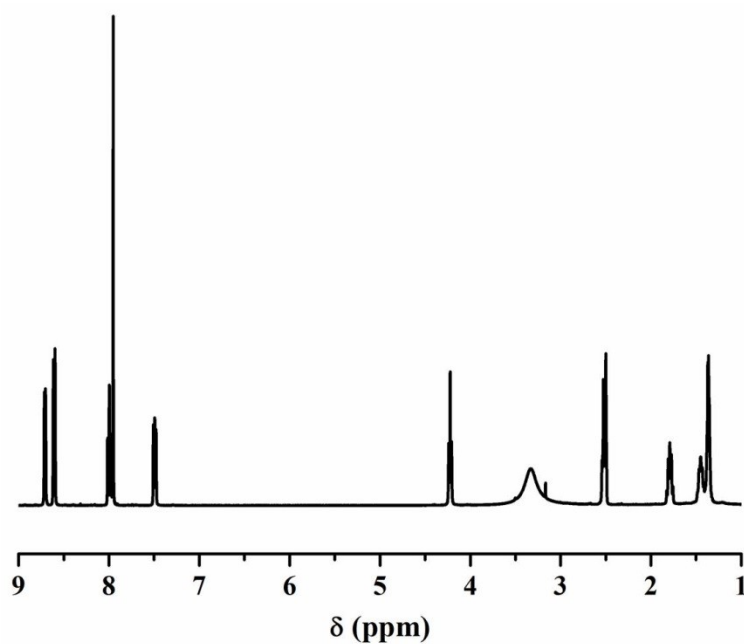


Figure S1. ¹H NMR spectra of tpy-NH₂ in DMSO-*d*₆.

The toughness of the film was calculated by integrating the tensile stress-strain curve using the following equation:

$$\text{Toughness} = \int_0^{\varepsilon_f} \sigma d\varepsilon \quad (\text{S1})$$

where ε is the strain, ε_f is the strain upon failure, and σ is stress.

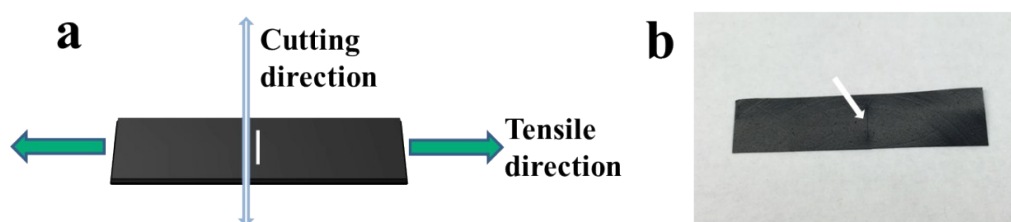


Figure S2. (a) A schematic diagram, and (b) a digital image of the film illustrating the cut made perpendicular to the tensile direction.

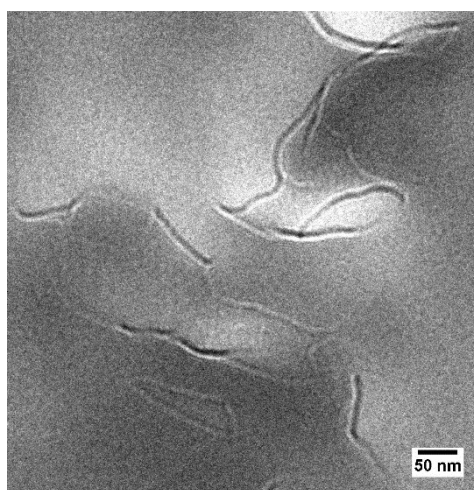


Figure S3. TEM images of the 0.5 wt% CNT/PU metallo-supramolecular polymer nanocomposite film.

The CNTs were uniformly distributed in the PU matrix.

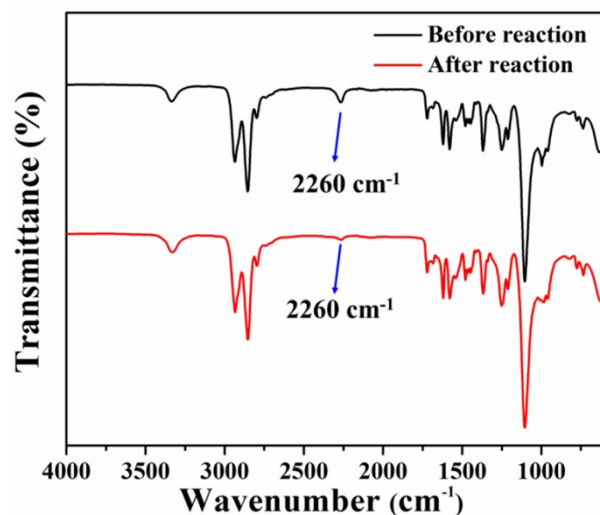


Figure S4. FTIR spectra of the isocyanate functionalized prepolymers before and after the conjugation of the tpy-NH₂ ligand.

The intensity of the characteristic peak of NCO at 2260 cm^{-1} decreased after the reaction with tpy-NH₂, but the peak was still present, indicating that the tpy-NH₂ was completely consumed by the excess amount of isocyanate groups.

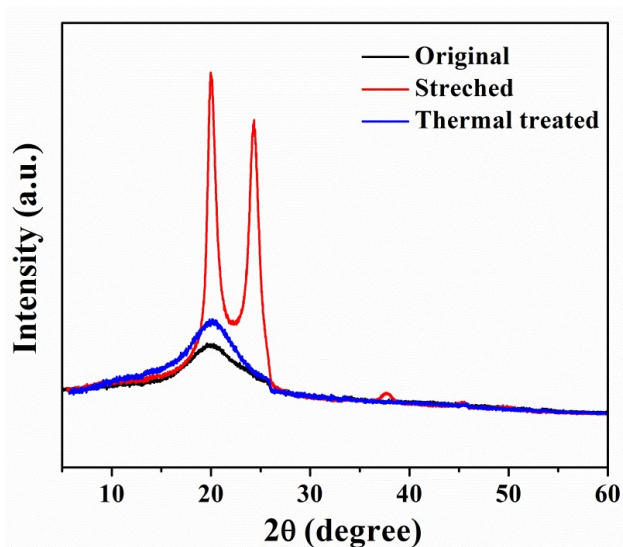


Figure S5. XRD patterns of the metallo-supramolecular CNT/PU polymer nanocomposite films before stretching, under stretching (strain = 500 %), and after stretching.

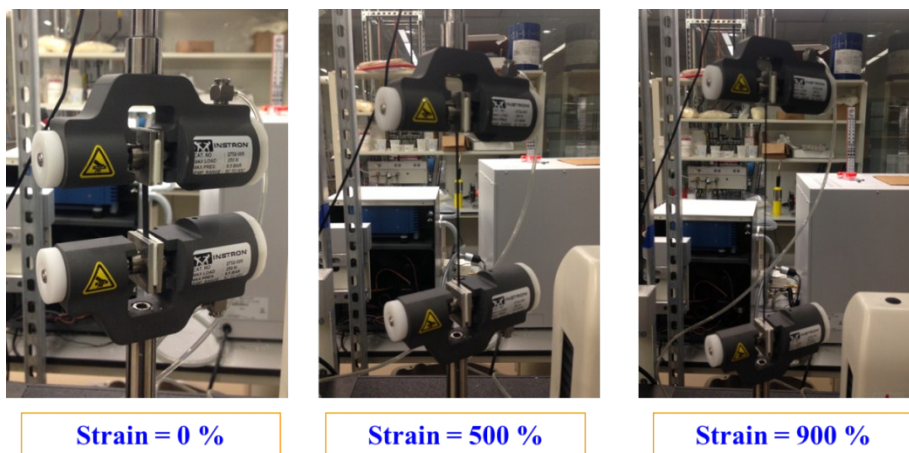


Figure S6. Optical images of the metallo-supramolecular CNT/PU polymer nanocomposite film being subjected to varying strains: 0%, 500%, and 900%.

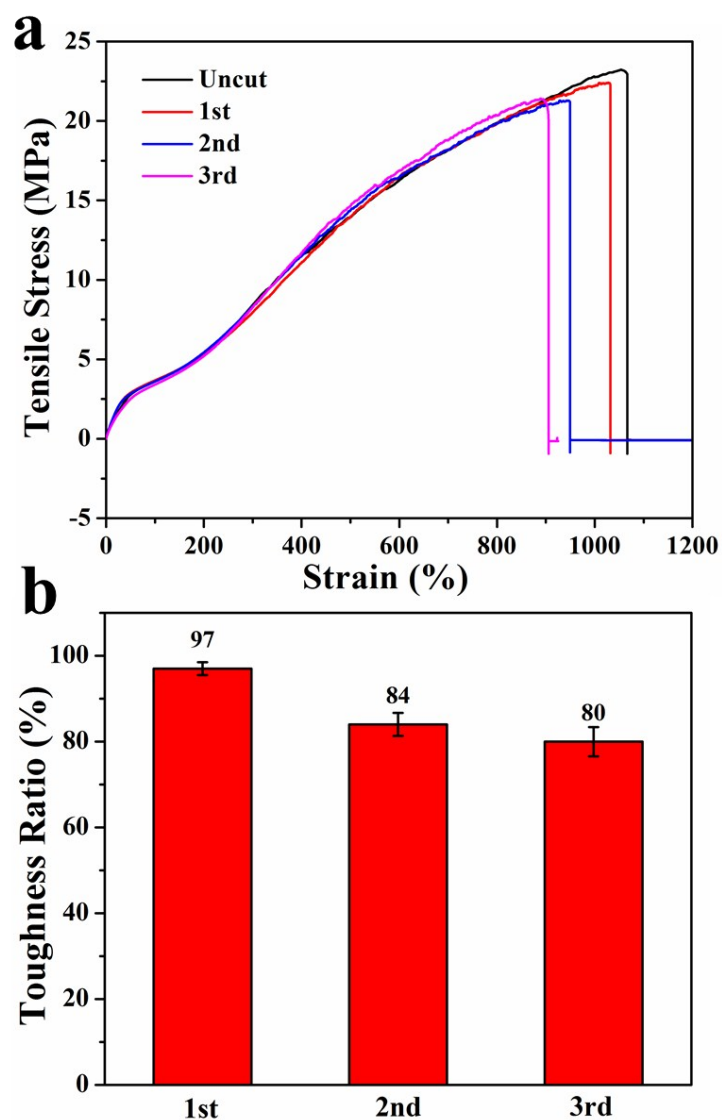


Figure S7. (a) The tensile stress-strain curves of the metallo-supramolecular films after being subjected to cyclic NIR light-assisted healing (i.e., the 1st, 2nd, and 3rd healing cycle). (b) The toughness ratios of the metallo-supramolecular films after being subjected to cyclic NIR light-assisted healing (i.e., the 1st, 2nd, 3rd healing cycle).

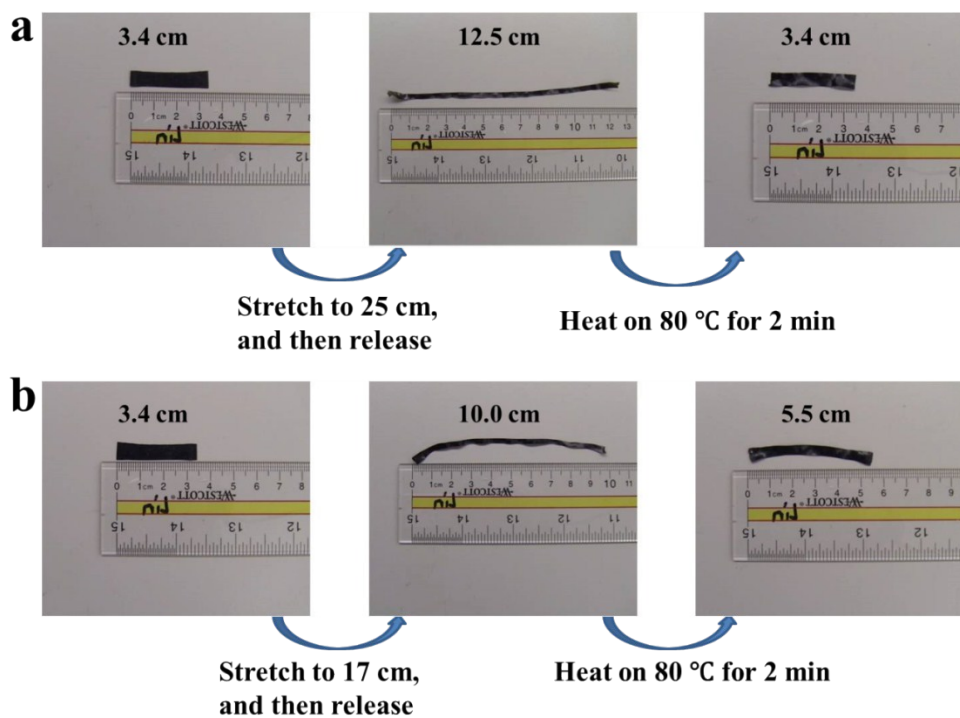


Figure S8. Shape memory tests on the (a) metallo-supramolecular film, and (b) control film.

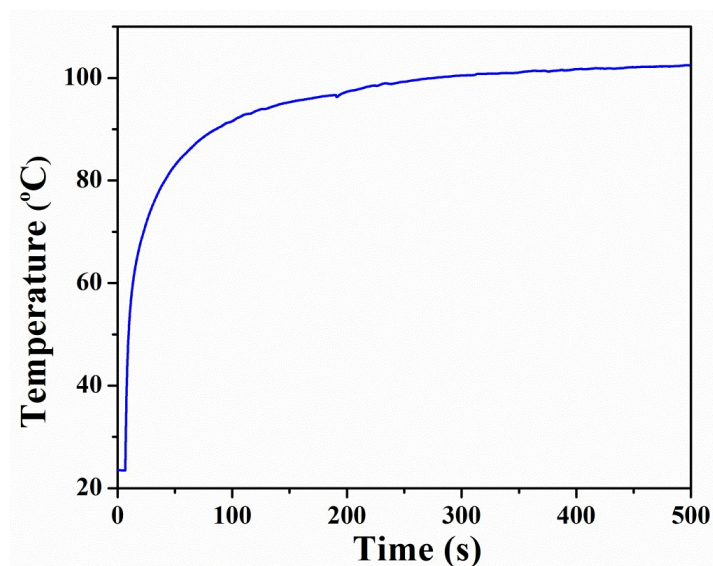


Figure S9. Temperature profiles of NIR-induced healing of the metallo-supramolecular film. The temperature of the metallo-supramolecular polymer nanocomposite film increased rapidly upon NIR irradiation (4.2 mW mm^{-2}) and reached a plateau ($\sim 100 \text{ }^\circ\text{C}$) after ~ 2 minutes. The temperature profile was collected on the back side of the film.

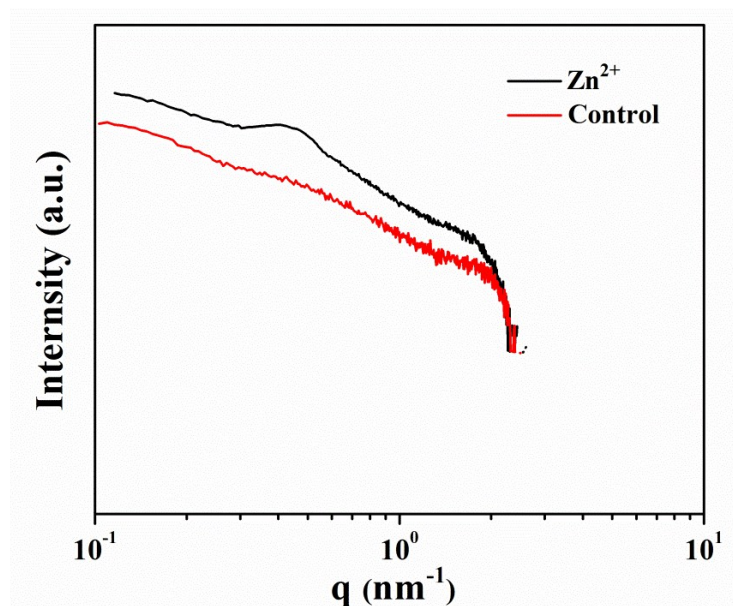


Figure S10. SAXS patterns of the metallo-supramolecular film and the control film.

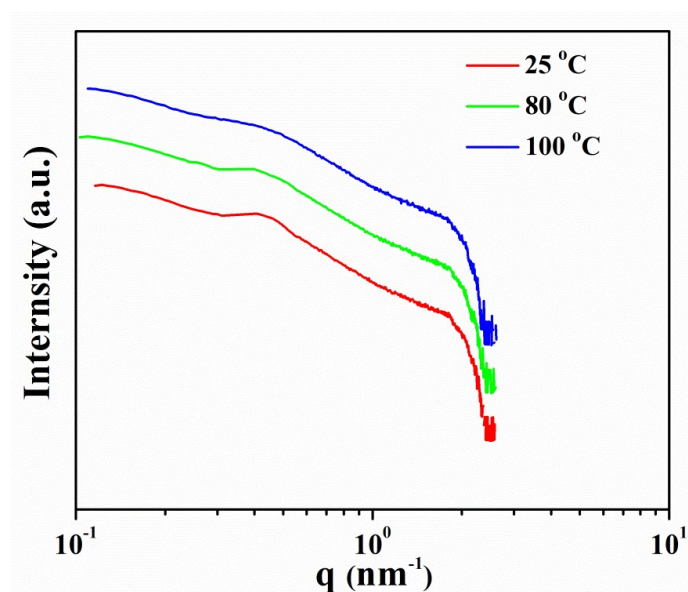


Figure S11. SAXS patterns of the metallo-supramolecular film at various temperatures (i.e., 25, 80, and 100 °C).

When the temperature rose from 25 °C to 80 °C, the scattering peak became broader and blunter, indicating partial dissociation of the Zn²⁺-terpyridine clusters. The peak intensity decreased further when the temperature increased to 100 °C.

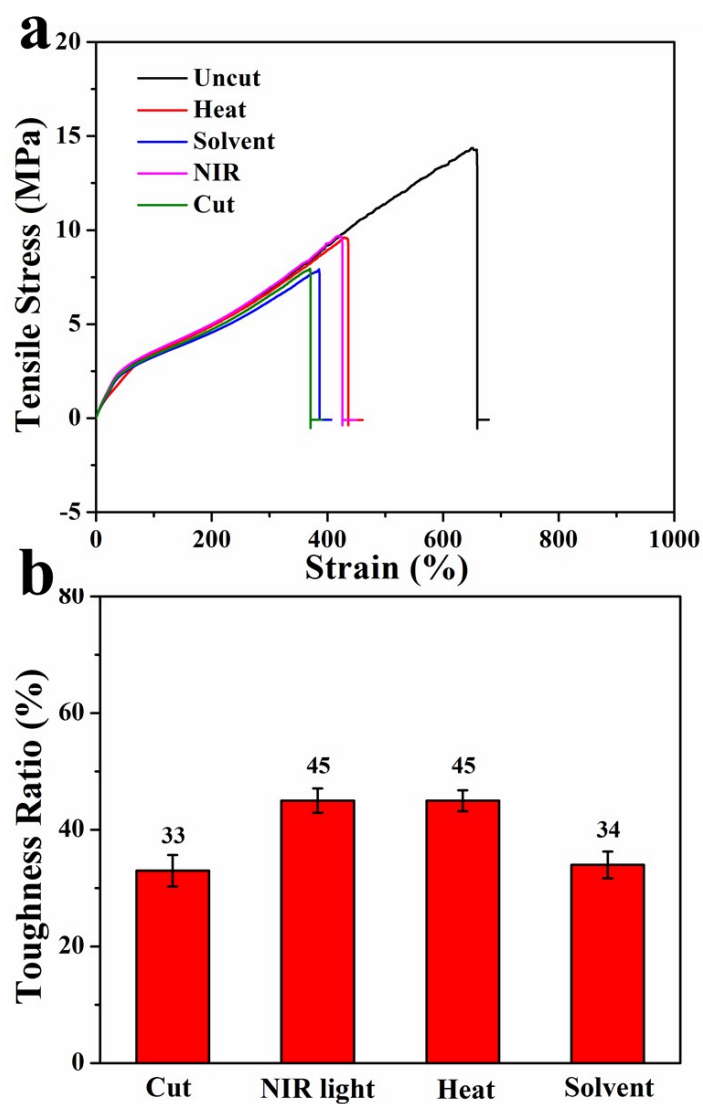


Figure S12. (a) Tensile stress-strain curves of the control films (i.e., the CNT/PU nanocomposite films without Zn^{2+} coordination) including the uncut film, NIR light-healed film, heat-healed film, solvent-healed film, and virgin cut film. (b) The toughness ratio of the control films including the cut film before any treatment, and cut film healed via NIR, heat, and solvent.

Table S1. Mechanical properties of the control films (i.e., the CNT/PU nanocomposite films without Zn²⁺ coordination) including the uncut film, NIR light-healed film, heat-healed film, solvent-healed film, and virgin cut film.

Sample	Young's modulus (MPa)	Tensile strain- at-break (%)	Tensile strength (MPa)	Material toughness (MPa)
Uncut	6.2 ± 0.3	658 ± 22	14.2 ± 0.3	51.2 ± 1.2
NIR light	6.2 ± 0.2	426 ± 20	9.5 ± 0.1	23.1 ± 1.2
Heat	4.7 ± 0.4	436 ± 18	9.4 ± 0.2	23.2 ± 1.1
Solvent	6.1 ± 0.3	386 ± 25	7.8 ± 0.4	17.6 ± 1.3
Cut	6.1 ± 0.6	371 ± 35	7.8 ± 0.8	16.8 ± 2.4