

Supplementary Information

Photo-driven metallo-supramolecular stress-free reversible shape memory polymer

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Materials:

Polycaprolactone diol ($M_n=10000$) was procured from Sigma-Aldrich. 4'-Chloro-2,2':6', 2''-Tripyridine was acquired from Aladdin. 1,5,7-triazabicyclo [4.4.0] dec-5-ene, 4'- 1,3-propanediol, triethylamine, ϵ -caprolactone, and acryloyl chloride were purchased from TCI. All chemicals were used as received.

Synthesis of 4'-[2-(3-hydroxy)propoxy]-2,2':6',2''-terpyridine:

The reaction scheme was shown in Figure S4a. 4'-chloro-2,2':6',2''-terpyridine (1 g), 1,3-propanediol (1.45 g), and potassium hydroxide (1 g), and anhydrous dimethyl sulfoxide (10 mL) were added into a 25mL flask and reacted under magnetic stirring at 70 °C for 48 hours. The produced liquid was poured into deionized water (50 mL) to yield a precipitate. The pH was adjusted to 6.7 by adding hydrochloric solution (10%). The liquid was subsequently removed by centrifugation and the remaining solid was vacuum dried at 70 °C for 48 hours. The obtained product was dissolved in methanol at 70 °C and recrystallized at about 0 °C. The crystalline solid was obtained by centrifugation and vacuum dried at 70 °C for 24 hours. This recrystallization-based purification process was repeated twice to yield the final product.

The product structure was confirmed in Figure S5.

Synthesis of polycaprolactone with a terpyridine end group ($M_n=5000$):

The reaction scheme was shown in Figure S4a. The hydroxyl-terminated terpyridine synthesized in the prior step (0.5 g), ϵ -caprolactone (8.6 g), and 1,5,7-triazabicyclo [4.4.0] dec-5-ene (0.5 wt%) were added into a 50 ml flask. The reaction was conducted at 120 °C in a nitrogen atmosphere for 10 hours. The resulting polymer was dissolved in toluene and precipitated in cold methanol. The obtained product was vacuum dried overnight at room temperature. The polymer structure was confirmed by $^1\text{H-NMR}$ spectrum (Figure S5) and the molecular weight was determined via the end group analysis.

Synthesis of TPyA:

The reaction scheme was shown in Figure S4a. 10 g of the polycaprolactone with a terpyridine end group obtained in the prior step, acryloyl chloride (0.54 g), and triethylamine (0.61 g) were co-dissolved in 50 mL toluene at 80 °C and reacted at this temperature for 20 hours. The purification followed the same process described in the predeceasing section and the product was confirmed by $^1\text{H-NMR}$ analysis (Figure S5).

Synthesis of Polycaprolactone diacrylate (PCLDA):

The reaction scheme was shown in Figure S4b. Polycaprolactone diol (30 g, $M_n=10000$), acryloyl chloride (1.63 g), and triethylamine (1.82 g) were co-dissolved in a 150 mL of toluene at 80 °C and reacted at this temperature for 20 hours. The purification followed the same process described in the predeceasing section and the product was confirmed by $^1\text{H-NMR}$ analysis (Figure S5).

Synthesis of TPy networks:

For the synthesis of TPy30, TPyA (1.5 g) and PCLDA (3.5 g) were dissolved in N, N-dimethylformamide (DMF, 5 g). Triethylamine (2 wt%) was added subsequently introduced. The solution mixture was transferred into a mold and reacted at 80 °C for 10 hours. The obtained gel film was dried in a vacuum oven at 70 °C for 10 hours. Other networks were synthesized likewise except that the ratio between the two macromonomers was varied accordingly.

Gel content tests:

A specimen was weighed before soaking in DMF for 24 hours. The swollen specimen was then vacuum dried for 24 hours at room temperature and weighed. The gel content was calculated based on the ratio between the final and initial weights.

Preparation of the supramolecular metallo-networks:

A weighed TPy network film (~1 g) was heated to 80 °C and immersed in a DMF solution (30 g) of FeSO₄ for 60 minutes, with the concentration of Fe²⁺ ion calculated based on a TPy: Fe molar ratio of 2. The free (non-coordinated) ions were removed by soaking the sample in a DMF solvent for 30 min. The final sample was dried in a vacuum oven at 70 °C overnight.

Programming of the reversible actuation:

A rectangular TPy network sample (15 mm×5 mm×0.4 mm) was uniaxially stretched to a target strain at 80 °C. The sample, which was held in its stretched form with a fixture, was crosslinked by doping with Fe²⁺ according to the process described in the predeceasing section.

Photo-thermal effect test:

Photo-thermal experiments were conducted with a xenon lamp (CEL-PE300L3A, 290 mW·cm⁻², Ceaulight company). The distance between a sample to the light source was fixed at 5 cm and the temperature was monitored by an infrared camera.

Characterization:

The Fe²⁺ content in a network film was determined through the Fe contents in the DMF solution before and after the doping experiment. The latter was determined by UV-vis analysis. All the thermal/thermomechanical analyses, along with the calculation of the reversible actuation strain, were conducted according to the procedures reported previously.

[1,2]

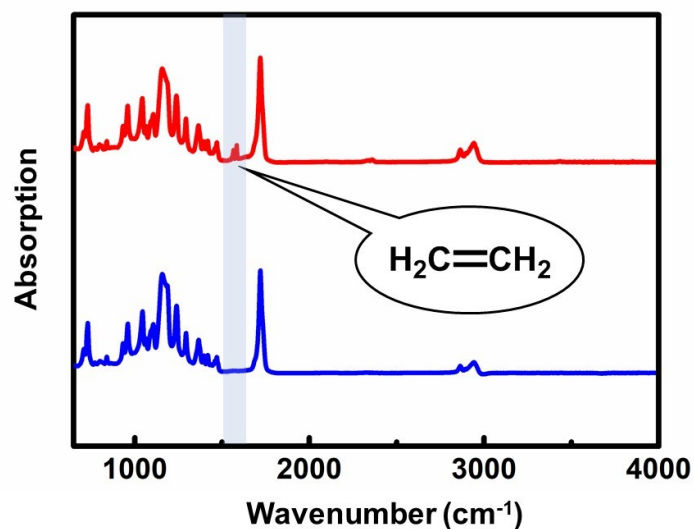


Figure S1. Infrared spectra of TPy30 before and after the network synthesis.

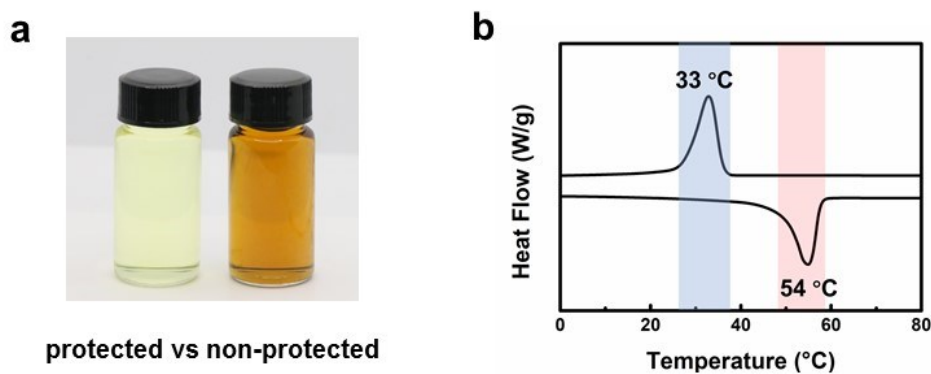


Figure S2. a) DMF solution of Fe^{2+} with and without HCl protection after 5 hours of storage under ambient condition. b) Full DSC scanning of TPy30 including cooling and heating curves.

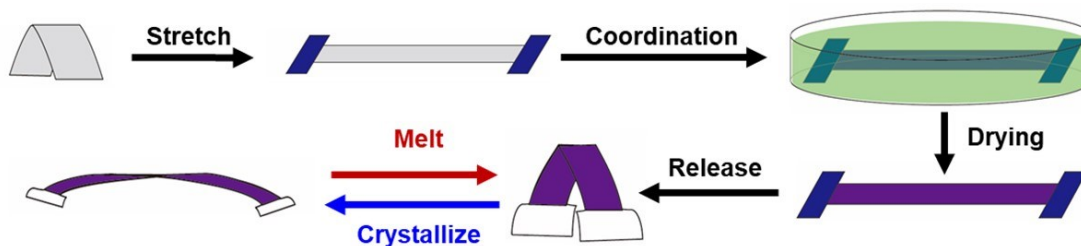


Figure S3. Preparation and programming of the crawling machine.

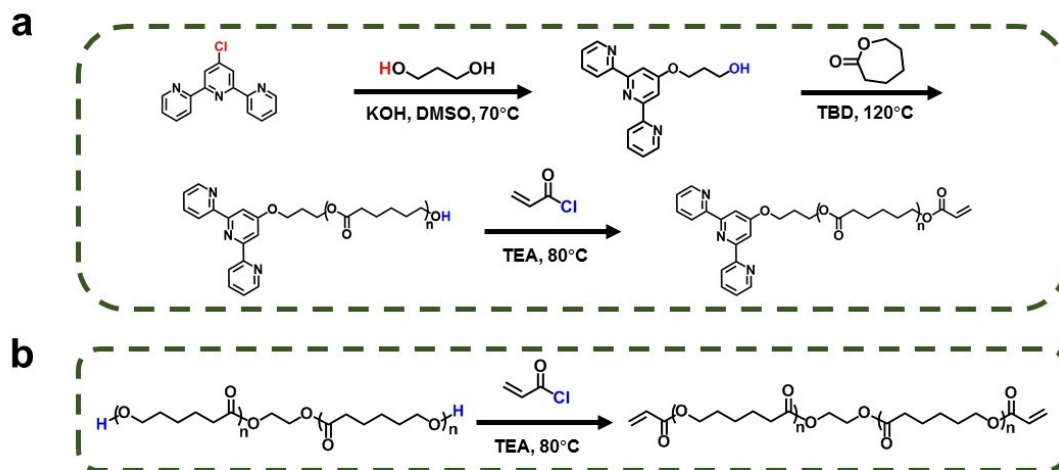


Figure S4. Synthetic steps for the network precursors.

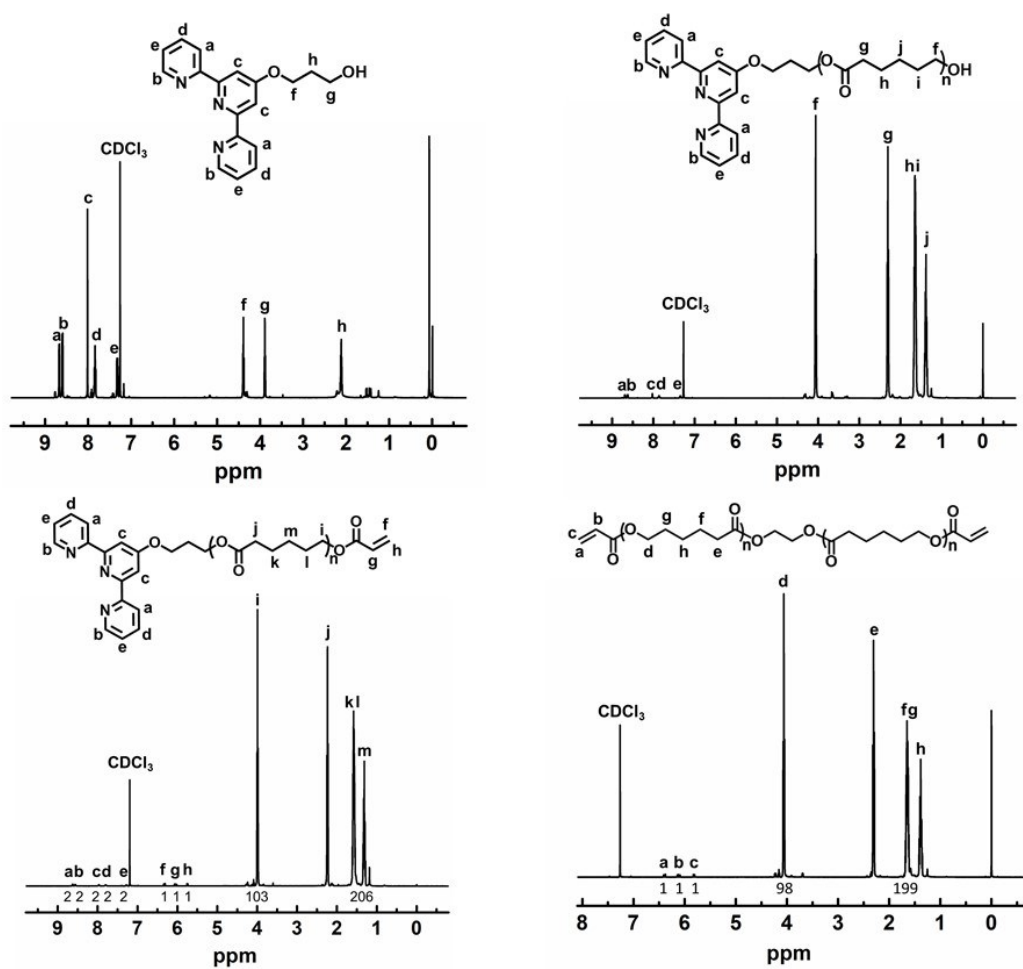


Figure S5. $^1\text{H-NMR}$ of the network precursors.

REFERENCES

- [1] B. Jin, H. Song, R. Jiang, J. Song, Q. Zhao, T. Xie, *Sci. Adv.* 2018, 4, eaao3865
- [2] H. Song, Z. Fang, B. Jin, P. Pan, Q. Zhao, T. Xie, *ACS Macro Lett.* 2019, 8, 682.

Supporting Videos

Movie S1: The live action of this soft machine.