

Supporting Information

Tough and body-temperature self-healing polysiloxane elastomers through building double physical crosslinking network via competing non-covalent interactions

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Synthesis of the PDMS–U. Typically, 8 g of bis (3-aminopropyl)-terminated poly (dimethylsiloxane) were mixed in 40 mL chloroform. Subsequently, the mixture was cooled to 0 °C by an ice bath and stirred for 1 h under nitrogen atmosphere. Then, a chloroform solution of 0.7 g TDI was added dropwise. The resulting mixture was stirred for 1 hour while the temperature was kept at 0 °C with ice water. The solution was then allowed to warm to room temperature and stirred for 4 days. After reaction, MeOH (15

mL) was added for complete removal of remained isocyanate and stirred for 30 minutes. Then, solution was concentrated to ½ of its volume and 60 mL MeOH was poured into it to precipitate. White precipitate-like viscous liquid appeared and the mixture was settled for 30 minutes. The upper clear solution was then decanted. 100 mL CHCl₃ was added to dissolve the product. The dissolution-precipitation decantation process was repeated for three times and the final product was subjected to vacuum evaporation to remove the solvent.

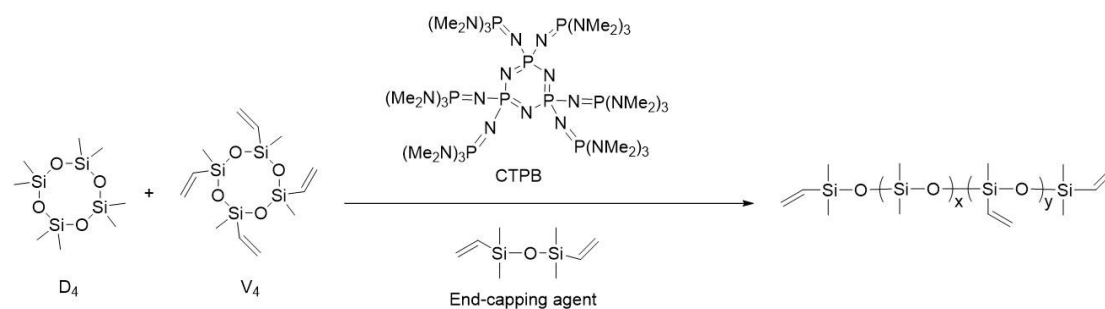
Synthesis of the PDMS precursor. The CTPB (0.02 mmol) and 1 mL toluene were added into a 10 mL flame-dried Schlenk flask under argon protection and were stirred for 10 min at room temperature. Predetermined V4, D4, DVDS and toluene were loaded into another 50 mL flame-dried Schlenk flask under argon protection. The concentration of monomers in toluene was 2.5 M. Polymerization was initiated by rapid addition of CTPB in toluene solution into the siloxane mixture *via* a syringe. After a desired period, the polymerization was quenched by precipitation with 50 mL methanol. The crude product was filtered, washed with methanol to remove the unreacted monomers, and then dried in a vacuum oven at 30 °C to a constant weight to afford the vinyl-containing PDMS precursor.

Synthesis of the PDMS-C (containing 15 mol% COOH). Precursor (2.5 g, 5 mmol of vinyl groups) was dissolved in 50 mL of THF and added to a mixture of MPA (1.6 g, 15.1 mmol) and DMPA (25 mg, 0.098 mmol). The mixed solution was degassed through bubbling argon in an ice/water bath for 20 min and irradiated under UV light at room temperature for 10 min. After the reaction was complete, the target product was

obtained by precipitation in water, washed with water three times to remove the unreacted MPA, and dried at room temperature under high vacuum.

Characterization

Gel Permeation Chromatography (GPC) measurements were measured using an Agilent 1260 (USA) with monodisperse polystyrene (PS) as the standard sample. THF was used as a mobile phase (flow rate: 1.0 mL min⁻¹); the column temperature was 40 °C. NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer. Deuterated chloroform (CDCl₃) was used as the reference.



Scheme S1 Ring opening polymerization of octamethylcyclotetrasiloxane (D₄) and tetravinyltetramethylcyclotetrasiloxane (V₄) catalyzed by the cyclic trimeric phosphazene base (CTPB).

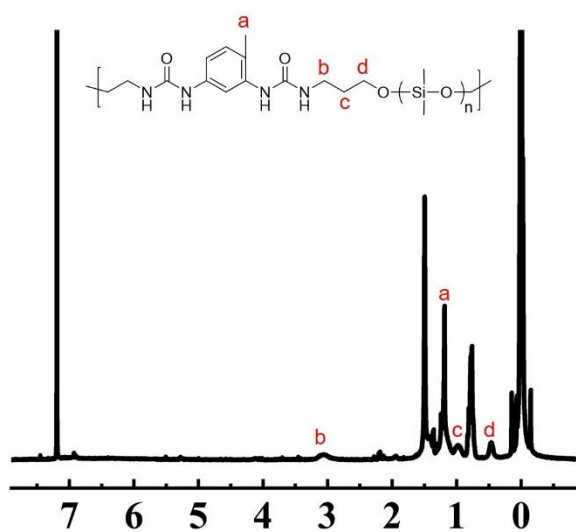


Fig. S1 ^1H NMR spectrum of PDMS-U in CDCl_3 .

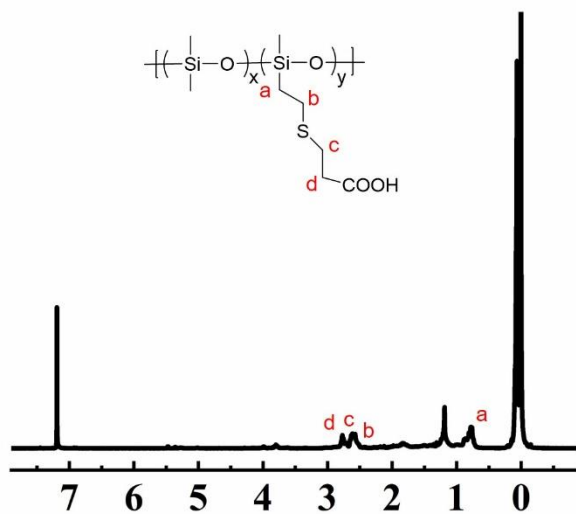


Fig. S2 ^1H NMR spectrum of PDMS-C in CDCl_3 .

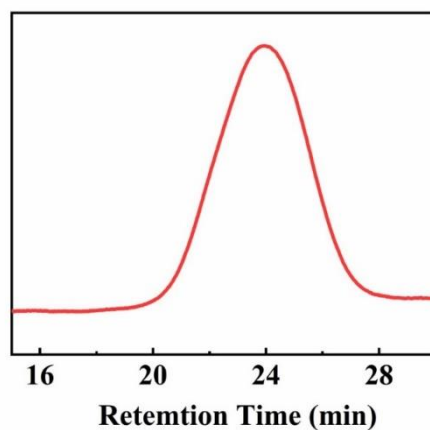


Fig. S3 GPC of PDMS-U.

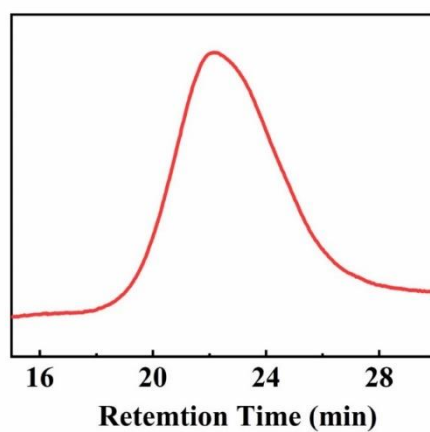


Fig. S4 GPC of PDMS-C.

Table S1 A summary for charge ratio of PDMS-U/PDMS-C_x/Zn²⁺ films

Materials	PDMS-C(g)	PDMS-U(g)	ZnCl ₂ (g)
PDMS-U/Zn ²⁺	0.00	16.31	1.23
PDMS-U/PDMS-C _{0.25} /Zn ²⁺	0.80	16.31	1.30
PDMS-U/PDMS-C _{0.3} /Zn ²⁺	1.00	16.31	1.33
PDMS-U/PDMS-C _{0.5} /Zn ²⁺	1.33	16.31	1.36
PDMS-U/PDMS-C _{0.7} /Zn ²⁺	2.00	16.31	1.43
PDMS-U/PDMS-C _{1.4} /Zn ²⁺	4.00	16.31	1.64

Table S2 A summary for charge ratio of PDMS-U/PDMS-C_x/Cu²⁺ films

Materials	PDMS-C(g)	PDMS-U(g)	CuCl ₂ (g)
PDMS-U/Cu ²⁺	0.00	16.31	1.22
PDMS-U/PDMS-C _{0.3} /Cu ²⁺	1.00	16.31	1.32
PDMS-U/PDMS-C _{0.5} /Cu ²⁺	1.33	16.31	1.35
PDMS-U/PDMS-C _{0.7} /Cu ²⁺	2.00	16.31	1.42
PDMS-U/PDMS-C _{1.4} /Cu ²⁺	4.00	16.31	1.62
PDMS-U/PDMS-C _{2.8} /Cu ²⁺	8.00	16.31	1.77

Table S3 A summary for charge ratio of PDMS-U/PDMS-C_x/Fe³⁺ films

Materials	PDMS-C(g)	PDMS-U(g)	FeCl ₃ (g)
PDMS-U/Fe ³⁺	0.00	16.31	1.46
PDMS-U/PDMS-C _{0.3} /Fe ³⁺	1.00	16.31	1.58
PDMS-U/PDMS-C _{0.5} /Fe ³⁺	1.33	16.31	1.63

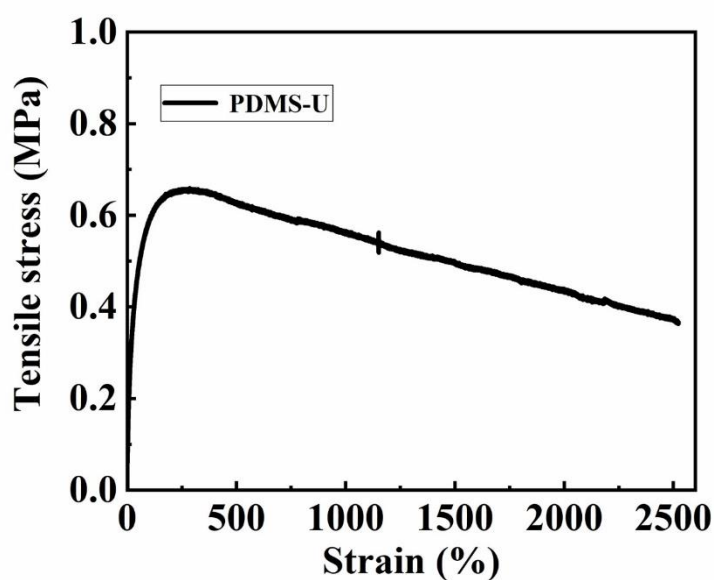


Fig. S5 Stress-strain curve of the PDMS-U film.

Table S4 A summary for mechanical properties of recently reported self-healing materials.

Materials	Maximum stress (MPa)	Fracture strain (%)	Source
PDMS-U/PDMS-C _{0.3} /Zn ²⁺	4.0	776	Our work
PDMS-TDI-AI-3	2.6	1700	Ref.21
P3K5K-SS-IP-AgFs	2.05	890	Ref.32
PPG-PDMS-Zn-0.5	0.98	5500	Ref.24
SiTAu-15 elastomer	2.0	1302	Ref.33
PBS polymer	0.4	1500	Ref.34

Table S5 Self-healing properties of the polysiloxane elastomers.

Films	4h Toughness (MJ m ⁻³)	6h Toughness (MJ m ⁻³)	8h Toughness (MJ m ⁻³)
PDMS-U/PDMS-C _{0.3} /Zn ²⁺	5.3	11.0	15.7
PDMS-U/PDMS-C _{0.5} /Cu ²⁺	4.7	14.0	14.5

Table S6 A summary for self-healing ability of recently reported self-healing materials.

Materials	Self-healing temperature (°C)	Self- healing time (h)	Self-healing efficiency (%)	Source
PDMS-U/PDMS- C _{0.3} /Zn ²⁺	37	8	98	Our work
PDMS-MPU-IU	25	48	78	Ref.20
Zn-Bpy-PDMS/AgNWs	25	24	90	Ref.35
APT-PDMS	105	24	91	Ref.36
PAPMS-M ₁₀ T ₂	25	12	83	Ref.37

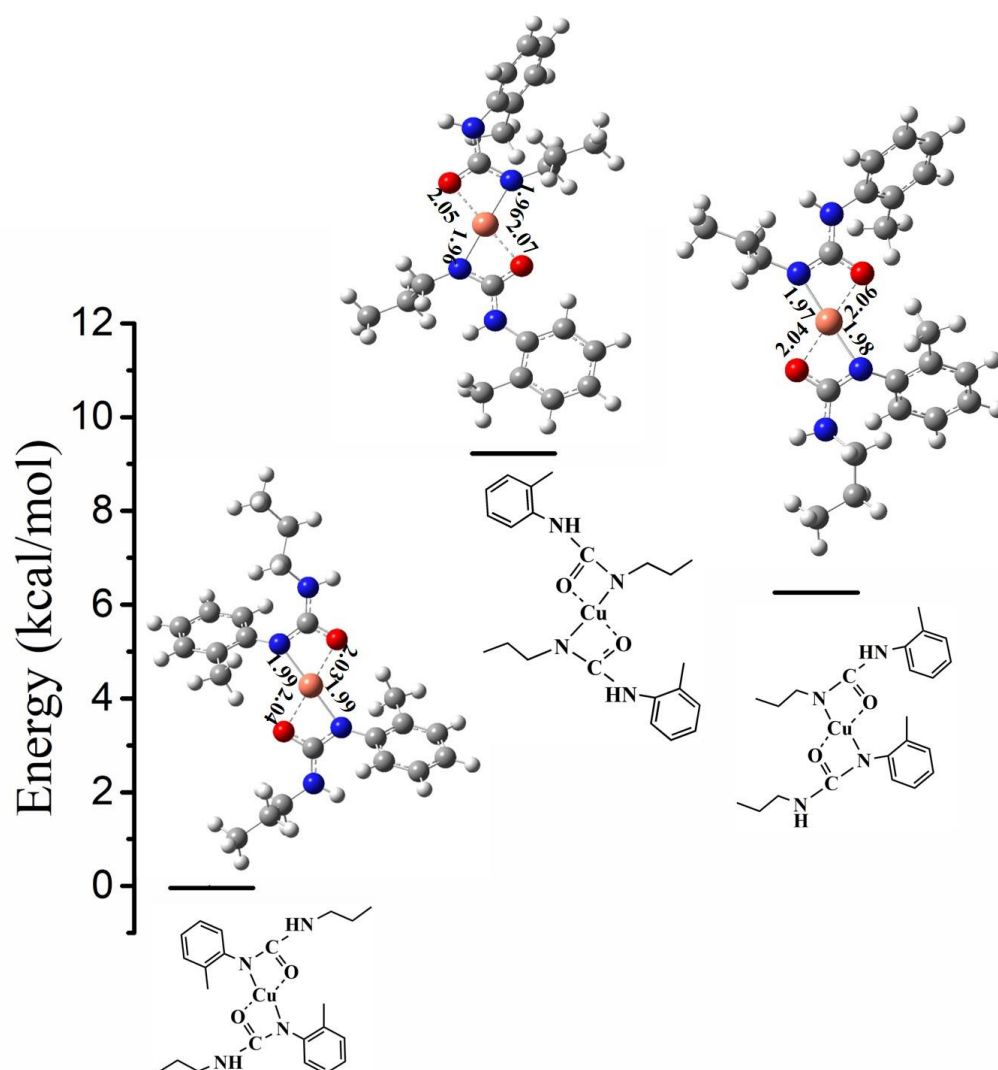


Fig. S6 DFT calculations. The calculation energies of Cu(urea)₂ complexes with different coordination modes, relative to the most stable geometry, which is assigned as 0 kcal mol⁻¹. Color scheme: carbon in gray, hydrogen in white, oxygen in red, nitrogen in blue and cuprum in brick red. Distances between selected atoms are given in Å.



Fig. S7 Photographs of the PDMS-U/PDMS-C_{0.5}/Cu²⁺ elastomer films before and after self-healing.

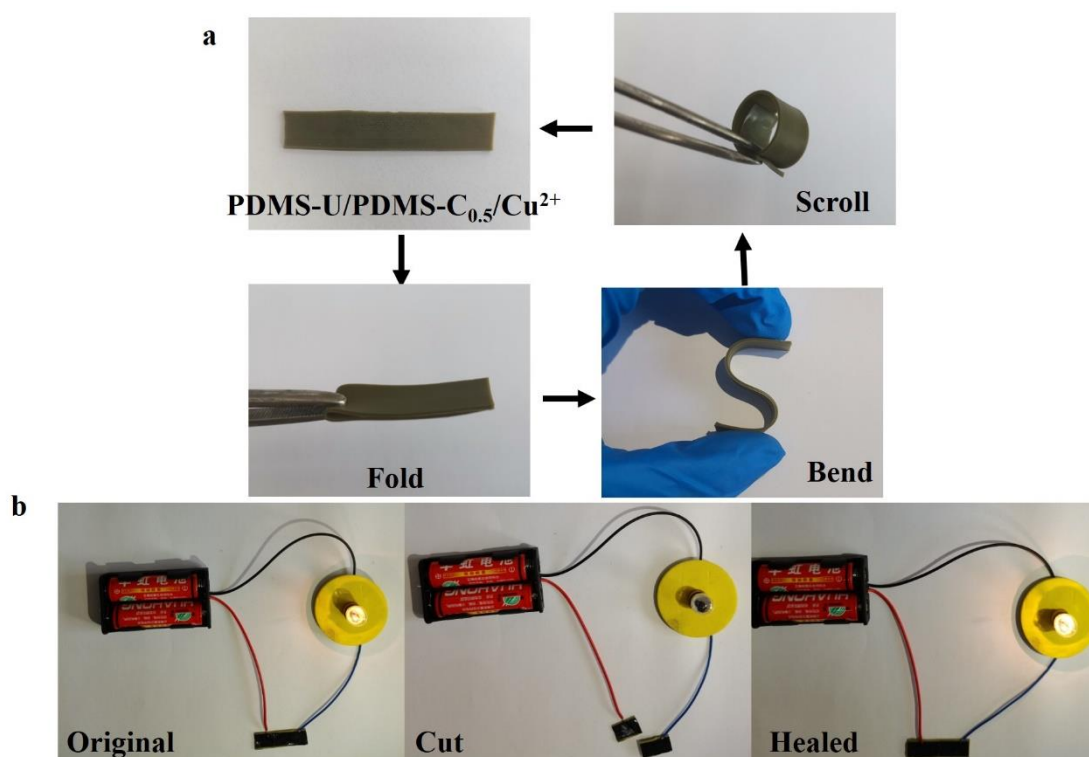


Fig. S8 (a) Flexibility of the PDMS-U/PDMS-C_{0.5}/Cu²⁺ film after bending, folding and scrolling. (b) Photographs of the healing process for the self-healing electrode with a bulb in the conductive circuit.