Supplementary Information (SI) for Journal of Materials Chemistry C.

A Mechanically Strong, Ultra-Tough and Room-Temperature Self-Healing Ionic Conductive Elastomer Based on Octopus-Like Physical Cross-linker Tannic Acid and Robust Polyurethane

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Experimental Section

1. Materials

Polycaprolactone diol (HO-PCL-OH, Mn~2000Da), isophorone diisocyanate (IPDI, 99%), dibutyltin dilaurate (DBTDL, 95%), 1-ethyl-3-methylimidazolidine bis(trifluoromethanesulfonyl)imide ([EMI][TFSI], 99%), hexamethylenediamine (HDA, 99%), tannic acid (TA, 99%) and green tea polyphenols (GTP, 98%) were obtained from Adamas-beta®. Adipic dihydrazide (AD, 99.0%) was supplied from aladdin®. N, N-dimethylformamide (DMF, 99.5%) was purchased from the General-reagent®. All chemicals were used as received without further purification.

2. Fabrication of the elastomer

2.1. Synthesis of PU elastomer (PU-AD)

Polycaprolactone diol 10.0 g (HO-PCL-OH, M_n=2000 g mol^{-1}, 5.0 mmol) was placed in a dry three-necked flask and heated under vacuum (<133 Pa) at 120 °C for 2 h to remove water. Subsequently, the temperature was reduced to 90 °C, and isophorone diisocyanate 2.3 mL (IPDI, 11 mmol) and 2-3 drops of and dibutyltin dilaurate (DBTDL) were added. The mixture was then stirred continuously for 3 h under a nitrogen atmosphere to yield the -NCO terminated prepolymer. Then, adipic dihydrazide 0.871 g (AD, 5.00 mmol) was dissolved in 80 mL DMF and added to the prepolymer mixture as a chain extender. Ultimately, a viscous and transparent PU-AD solution was produced following a 15 h reaction at 90 °C. Then most of the solvent was removed under reduced pressure. The resulting solution was poured into polytetrafluoroethylene (PTFE) molds and heated in an oven at 80 °C for 12 h to remove the remaining solvent. The obtained film was dried in a vacuum oven at 80 °C for another 24 h to afford the final PU-AD elastomer.

2.2. Preparation of PU-IL elastomers

A typical procedure for the preparation was as follows. 1-ethyl-3-methylimidazolidine bis(trifluoromethanesulfonyl)imide ([EMI][TFSI]) and PU-AD were dissolved in an appropriate amount of DMF at a mass ratio of 1:1 DMF to obtain a mixture solution. Then, most of the solvent was removed under reduced pressure. The resulting solution was poured into polytetrafluoroethylene (PTFE) molds and heated in an oven at 80 °C for 12 h to remove the remaining solvent. The obtained film was dried in a vacuum oven at 80 °C for 12 h to afford the transparent PU-100IL elastomer.

2.3. Preparation of PU-IL-TA elastomers

A typical procedure for the preparation was as follows. Tannic Acid (TA), [EMI][TFSI] and PU-AD were dissolved in an appropriate amount of DMF at a mass ratio of 1:10:10, and the mixture was stirred for 6 h at room temperature. Then, most of the solvent was removed under reduced pressure. The resulting solution was poured into polytetrafluoroethylene (PTFE) molds and heated in an oven at 80 °C for 12 h to remove the remaining solvent. The obtained film was dried in a vacuum oven at 80 °C for 12 h to afford the transparent PU-100IL-10TA.

2.4. Preparation of PU/HDA-100IL-10TA elastomers

Polycaprolactone diol 10.0 g (HO-PCL-OH, M_n=2000 g mol^{-1}, 5.0 mmol) was placed in a dry three-necked flask and heated under vacuum (<133 Pa) at 120 °C for 2 h to remove water. Subsequently, the temperature was reduced to 90 °C, and isophorone diisocyanate 2.3 mL (IPDI, 11 mmol) and 2-3 drops of and dibutyltin dilaurate (DBTDL) were added. The mixture was then stirred continuously for 3 h under a nitrogen atmosphere to yield the -NCO terminated prepolymer. Then, hexamethylenediamine 0.581 g (HDA, 5.00 mmol) was dissolved in 30 mL DMF and added to the prepolymer mixture as a chain extender. Ultimately, a viscous and transparent PU-HDA solution was produced following a 15 h reaction at 50 °C. Then most of the solvent was removed under reduced pressure. The resulting solution was poured into polytetrafluoroethylene (PTFE) molds and heated in an oven at 80 °C for 12 h to remove the remaining solvent. The obtained film was dried in a vacuum oven at 80 °C for another 24 h to afford the final PU-DH elastomer.

A typical procedure for the preparation was as follows. Tannic Acid (TA), [EMI][TFSI] and PU-DH were dissolved in an appropriate amount of DMF at a mass ratio of 1:10:10, and the mixture was stirred for 6 h at room temperature. Then, most of the solvent was removed under reduced pressure. The resulting solution was poured into polytetrafluoroethylene (PTFE) molds and heated in an oven at 80 °C for 12 h to remove the remaining solvent. The obtained film was dried in a vacuum oven at 80 °C for 12 h to afford the transparent PU/DH-100IL-10TA.

2.5. Preparation of PU-100IL-GTP elastomers

A typical procedure for the preparation was as follows. Green tea polyphenols (GTP), [EMI][TFSI] and PU-AD were dissolved in an appropriate amount of DMF at a mass ratio of 1x:10:10 (x is the mass multiple of GTP having the same -OH content as TA), and the mixture was stirred for 6 h at room temperature. Then, most of the solvent was removed under reduced pressure. The resulting solution was poured into polytetrafluoroethylene (PTFE) molds and heated in an oven at 80 °C for 12 h to remove the remaining solvent. The obtained film was dried in a vacuum oven at 80 °C for 12 h to afford the transparent PU-100IL-GTP.

3. Characterization

3.1. General characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet iS50, Thermo Fisher Scientific, China), proton-1 nuclear magnetic resonance (^{1}H-NMR) (AVANCE III 600, Bruker, Swit) were used to determine the chemical composition of the obtained elastomers. The molecular weight of PU-AD and its polydispersity index were measured on a Viscoteck TDAmax gel permeation chromatography (GPC) instrument, with tetrahydrofuran as the eluent. The UV-vis spectra were recorded on a Lambda950 spectrophotometer. Thermal stability analysis was conducted on a TGA/DSC3+ thermogravimetric analyzer (TGA) under an N_2 atmosphere. Each sample with a weight of ~10 mg was heated from 25°C to 800°C at a ramping rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) measurements were performed under an N_2 flow rate of 50 mL min-1 using a DSC Q2000 differential scanning calorimeter operating at a heating/cooling rate of 10°C min^{-1}, where the second heating scan was considered the real scan. The stress-strain curves were measured at room temperature (ca. ~20% relative humidity) using a HY-0580 universal testing machine with a stretching speed of 100 mm min^{-1}. Conductivity was measured using an electrochemical workstation. The electrochemical testing was conducted using two circular copper plates with a radius of 1 cm as electrodes, with the sample size being larger than the area of the copper plates. The plates were clamped using battery clips, and the device was then connected to the workstation for testing. Rheological experiments were conducted using a MCR 302 rheometer with 25 mm parallel plate geometry. X-ray diffraction (XRD) patterns were recorded using a Rigaku Smart Lab SE X-ray diffractometer with Cu Kα radiation. The data were collected between 3 and 80° with a scanning speed of 20° min^{-1}. Small-angle X-ray scattering (SAXS) maps were analyzed using a SAXSess MC 2 type diffractometer in the range of 0.07-2.5 nm^{-1}. Atomic Force Microscope (AFM) was recorded using a Mutimode 8 to observe microphase separation structure of elastomer samples. To monitor the change in resistance during deformation, the two ends of the PU-100IL-10TA was connected to a conductive copper tape. Then the conductive copper tape was connected to a source meter unit (KEYSIGHT 34401A, Keysight Technologies, USA) to monitor the change of the resistance during the deformation. Digital images and videos were captured using a Xiaomi 13 cell phone.

3.2. True Stress-Strain Curve

Define the true stress at different strains by considering a constant sample volume between fixtures (σ_{True}) . Calculate the true stress according to the following equation (1)：

$$\sigma_{True} = \sigma_n \times (\varepsilon + 1) \tag{1}$$

The symbol ε represents the nominal strain (mm mm^{-1})， σ_n is the nominal stress at the corresponding strain.

3.3. Fracture energy

By the Green-Smith method, the fracture energy of the elastomer is calculated according to the following equation (2)：

$$G_c = \frac{6Wc}{\sqrt{\lambda_c}} \tag{2}$$

In this context, λ_c represents the strain at break of the notched sample, c denotes the length of the notch, and W signifies the energy calculated by integrating the stress-strain curve of the unnotched sample up to λ_c. In this experiment, the tensile speed was set at 100 mm min^{-1}.

3.4 Healing efficiency

The healing efficiency is generally determined by measuring the tensile strength or toughness of the material before and after healing. The healing efficiency based on tensile strength (η_s) and toughness (η_t) were both measured and calculated. The formulas are used as follows

$$\eta_s = \frac{Stress\ (healed)}{Stress\ (initial)} \times 100\% \qquad \eta_t = \frac{Toughness\ (healed)}{Toughness\ (initial)} \times 100\%$$

Here, Stress (healed) and Toughness (healed) represent the tensile strength and toughness after healing, respectively. Stress (original) or Toughness (original) represents the original tensile strength and toughness, respectively.

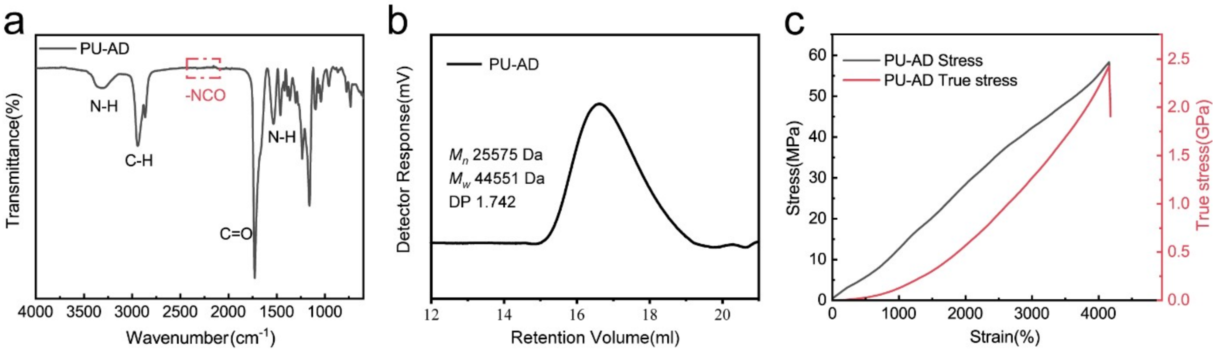

Fig. S1 (a) ATR-FTIR plot of PU-AD. (b) GPC profile of PU-AD. (c) Typical nominal (black) and true (red) stress-strain curves for PU-AD elastomer.

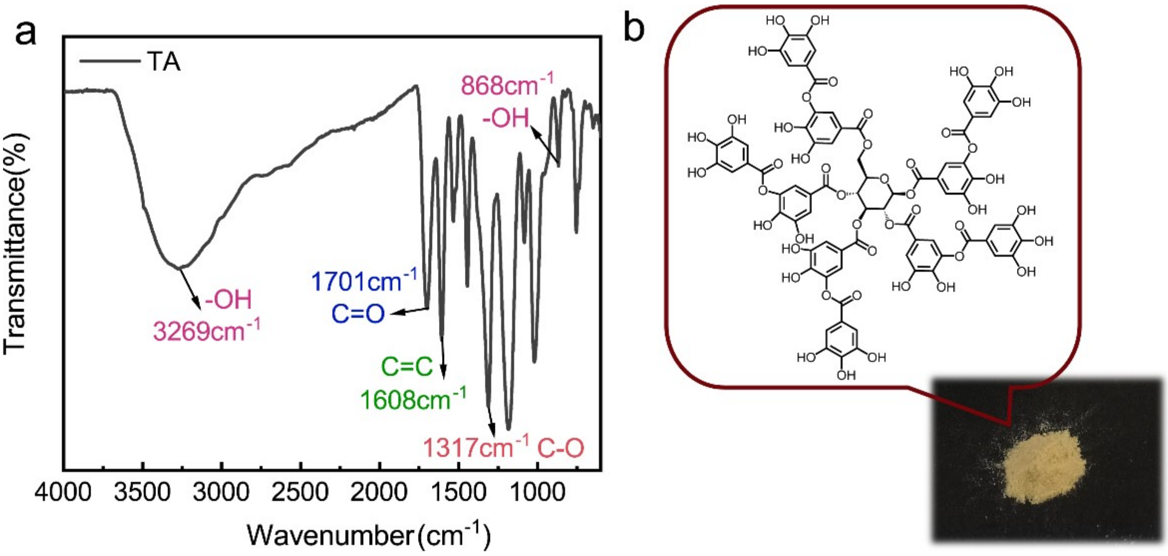

Fig. S2 (a) FTIR spectrum of TA. (b) Structure of TA.

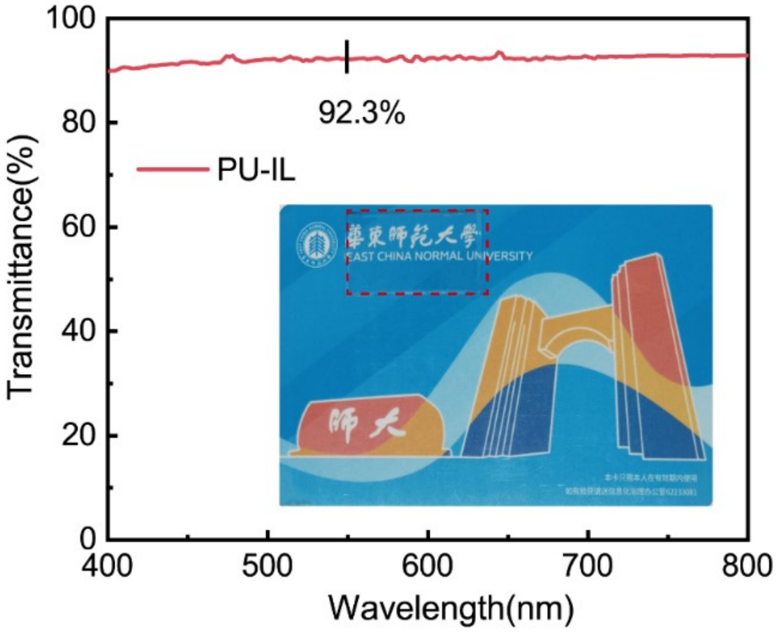

Fig. S3 UV–*vis* spectrum and digital photograph of PU-IL with thickness ~0.2 mm.

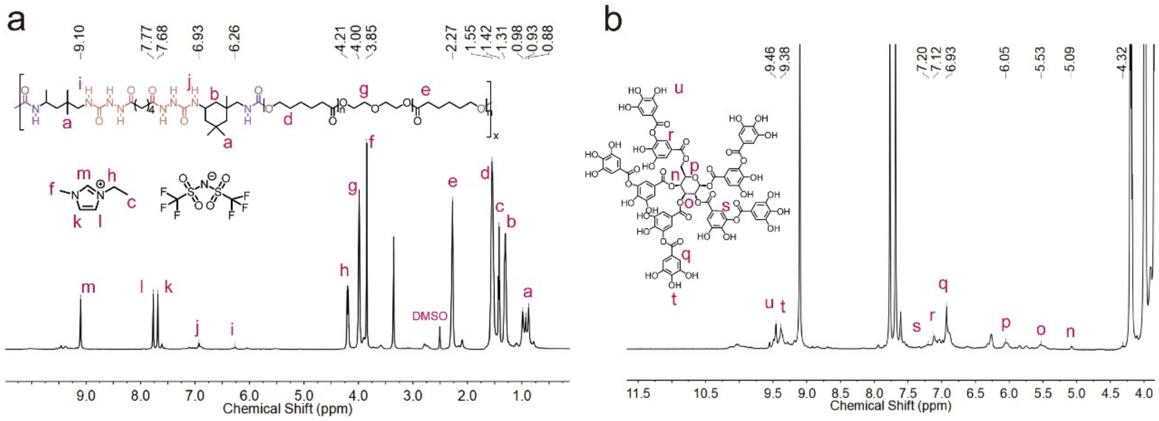

Fig. S4 (a) ^{1}H NMR spectrum of PU-IL-TA elastomer in DMSO-d_6. (b) Magnified ^{1}H NMR spectrum of PU-IL-TA elastomer in DMSO-d_6 (4.0-10.5 ppm).

Table S1. The deconvolution subpeak attribution of C=O absorption bands in the ATR-FTIR spectra of PU-AD and PU-200IL elastomers

Assignment		**Wavenumber(cm^{-1})**		**Area (%)**	
		PU-AD	**PU-200IL**	**PU-AD**	**PU-200IL**
υ (C=O) ester urethane amide	Free	1733	1732	27.2	35.5
	H-bonded (Disordered)	1718	1720	20.9	20.3
	H-bonded (Ordered)	1703	1704	17.4	15.3
υ (C=O) urea amide	Free	1683	1688	13.3	14.4
	H-bonded (Disordered)	1662	1669	12.1	7.5
	H-bonded (Ordered)	1641	1651	9.1	7.0

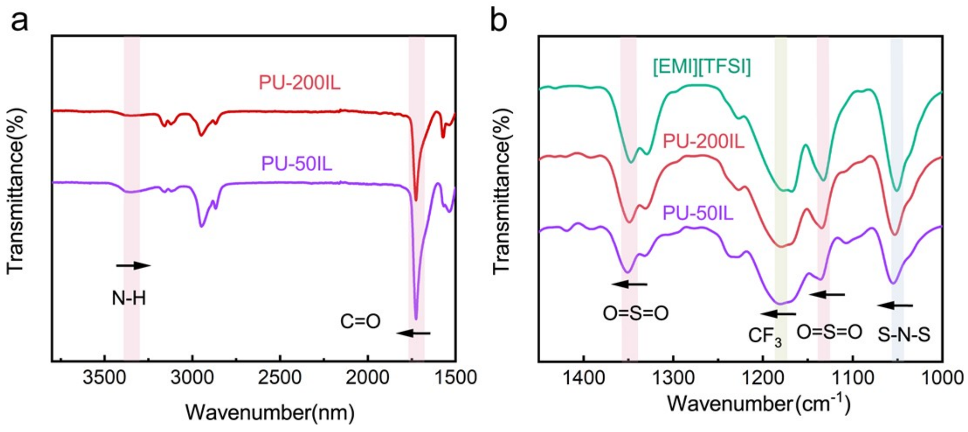

Fig. S5 (a) ATR-FTIR spectra of PU-50IL and PU-200IL in the region of 1500-3800 cm^{-1}. (b) ATR-FTIR spectra of PU-50IL, PU-200IL and [EMI][TFSI] in the region of 1000-1600 cm^{-1}.

Table S2. The characteristic absorptions in the ATR-FTIR spectra of IL, PU-50IL and PU-200IL elastomers

Assignment			Wavenumber(cm^{-1})		
			IL	**PU-50IL**	**PU-200IL**
PU		N-H		3355	3373
		C=O		1726	1724
IL	[EMI]	C-H	3159	3158	3156
IL	[EMI] [TFSI]	C=N	1574	1566	1571
		O=S=O asymmetric	1346	1350	1348
	[TFSI]	CF_3	1177	1181	1179
		O=S=O symmetric	1132	1135	1133
		S–N–S	1050	1055	1053

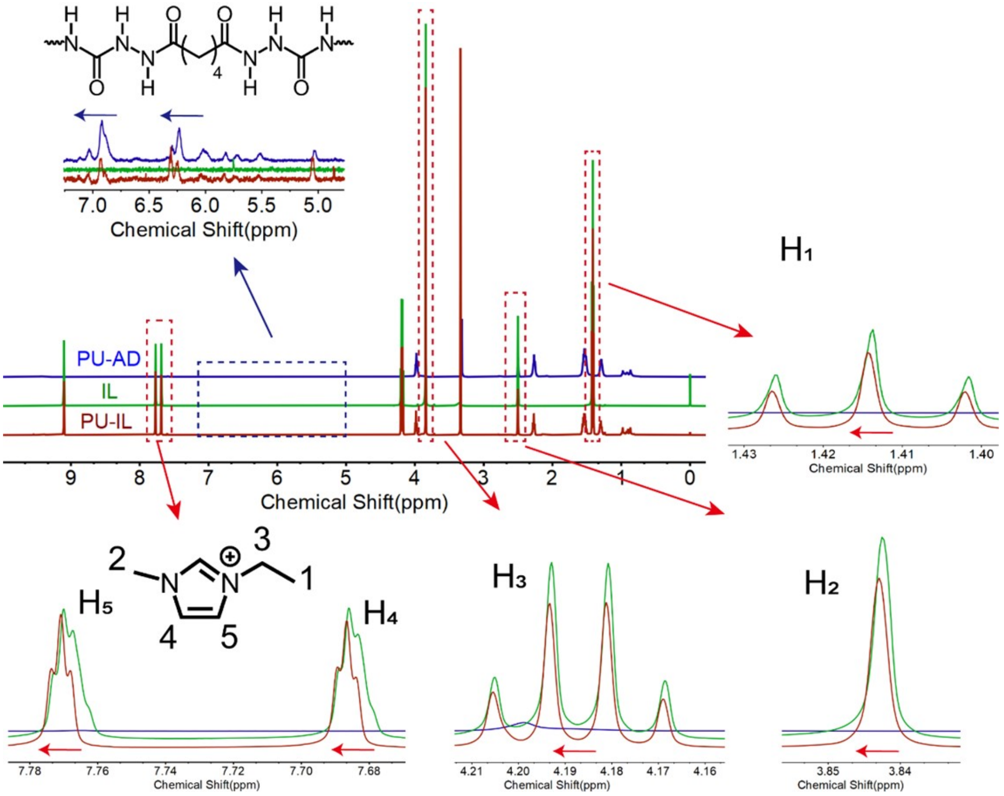

Fig. S6 ^{1}H NMR spectra of PU-AD, IL and PU-IL elastomers in DMSO-d_6.

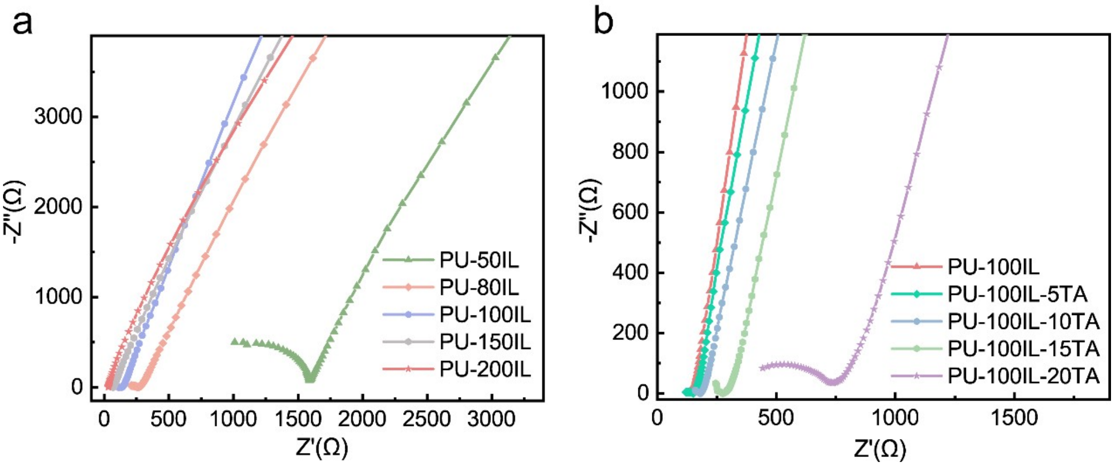

Fig. S7 (a) Nyquist plot of PU-IL at room temperature. (b) Nyquist plot of PU-IL-TA at room temperature.

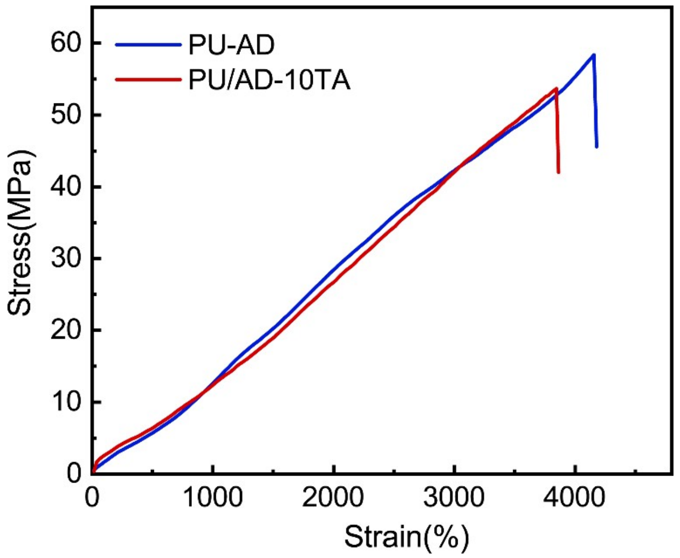

Fig. S8 The typical stress-strain curves of PU-AD and PU/AD-10TA.

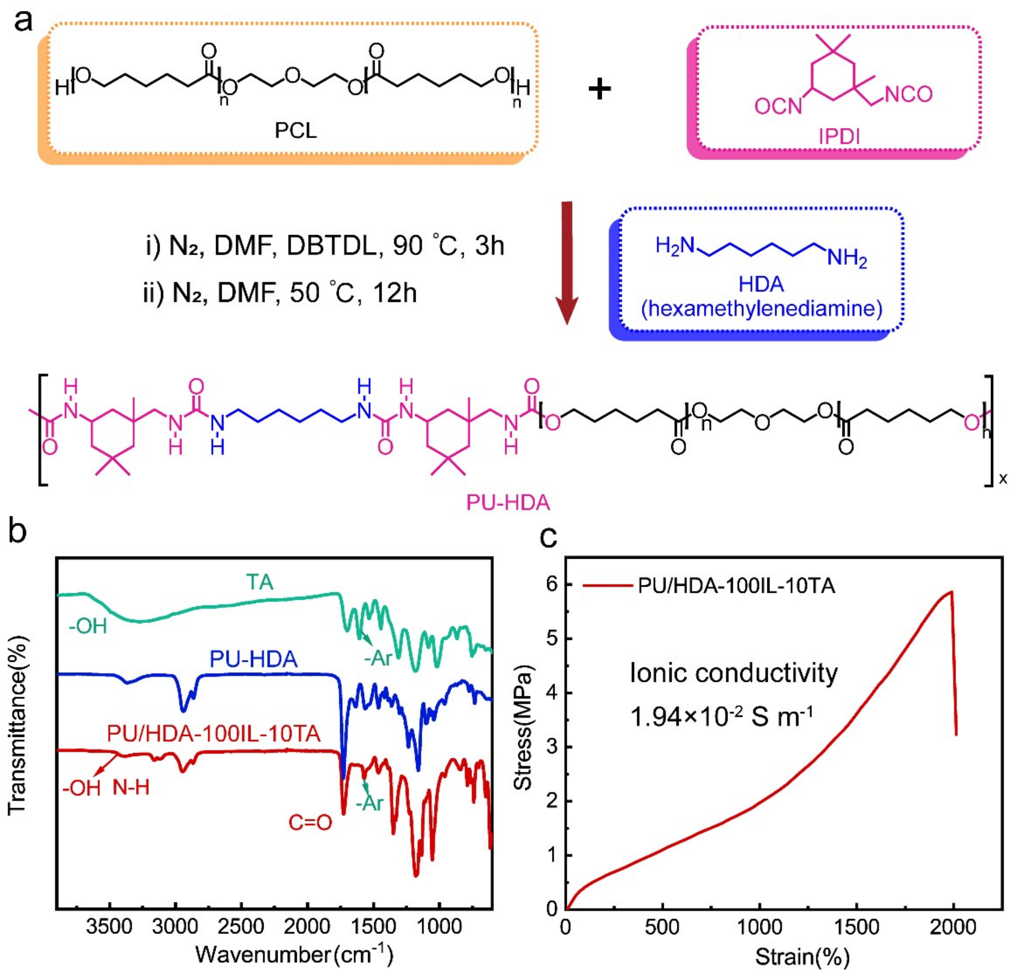

Fig. S9. (a) Synthesis of PU-HDA elastomer. (b) ATR-FTIR spectra of PU-HDA and PU/HDA-100IL-10TA. (c)The typical stress-strain curves and ionic conductivity of

PU/HDA-100IL-10TA.

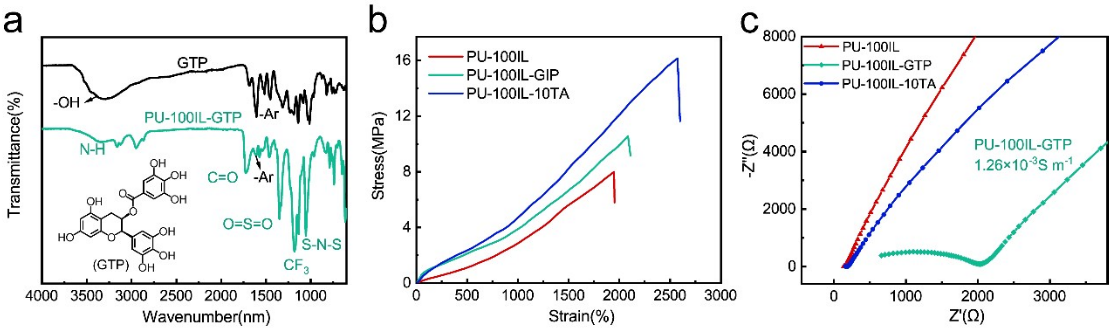

Fig. S10 (a) ATR-FTIR spectra of GTP and PU-100IL-GTP. (b) Nyquist plot of PU-100IL, PU-100IL-GTP and PU-100IL-10TA at room temperature. (c)The typical stress-strain curves of PU-100IL, PU-100IL-GTP and PU-100IL-10TA.

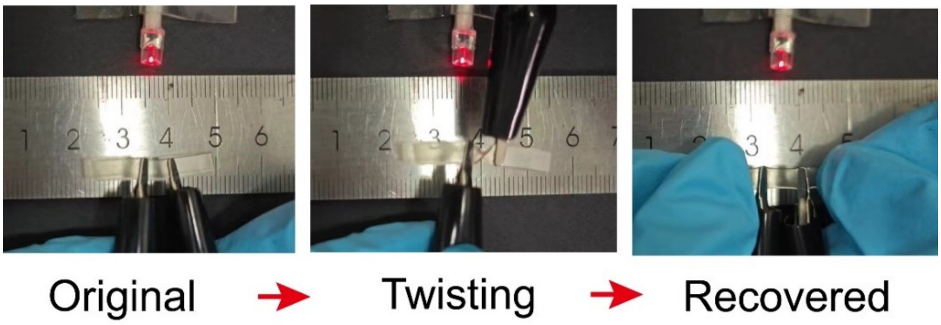

Fig. S11 Digital photographs of PU-100IL-10TA acting as a conductor and lighting a LED bulb.

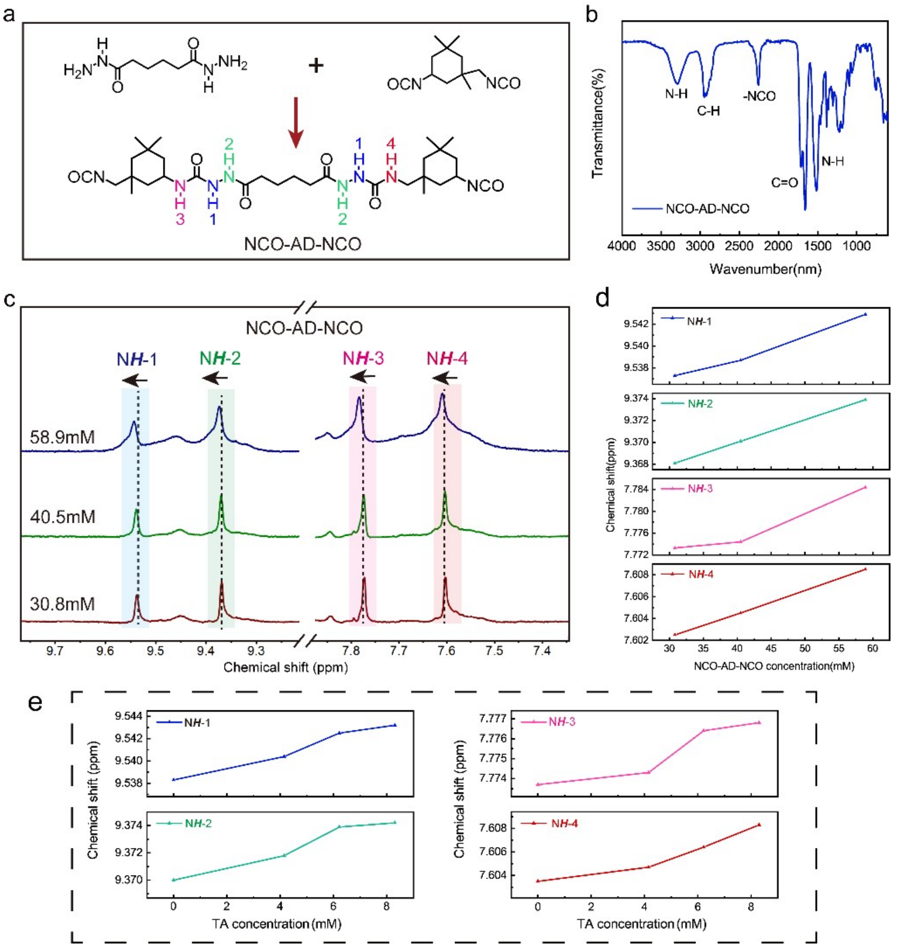

Fig. S12 (a) Synthesis of NCO-AD-NCO model compound. (b) ATR-FTIR spectra of NCO-AD-NCO**.** (c) ^{1}H NMR spectra of different concentrations of NCO-AD-NCO in DMSO-d_6 (600 MHz, 25°C, 1mM=1×10^{-3} mol L^{-1}). (d) Curves of chemical shifts of N***H***-1, N***H***-2, N***H***-3 and N***H***-4 in NCO-AD-NCO at different concentration of NCO-AD-NCO in ^{1}H NMR spectra. (e) Curves of chemical shifts of N***H***-1, N***H***-2, N***H***-3 and N***H***-4 in NCO-AD-NCO at different concentration of TA in ^{1}H NMR spectra.

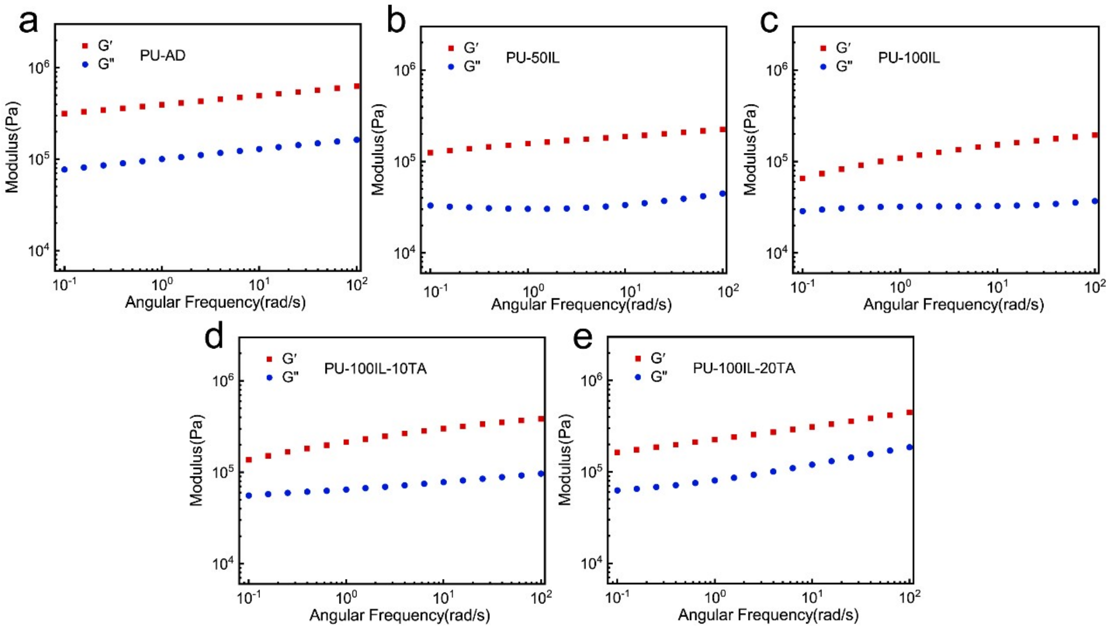

Fig. S13 Dynamic sweep tests of storage modulus G' and loss modulus G" of elastomers at a shear strain of 1%. (a) PU-AD elastomer. (b) PU-50IL elastomer. (c) PU-100IL elastomer. (d) PU-100IL-10TA elastomer. (e) PU-100IL-20TA elastomer.

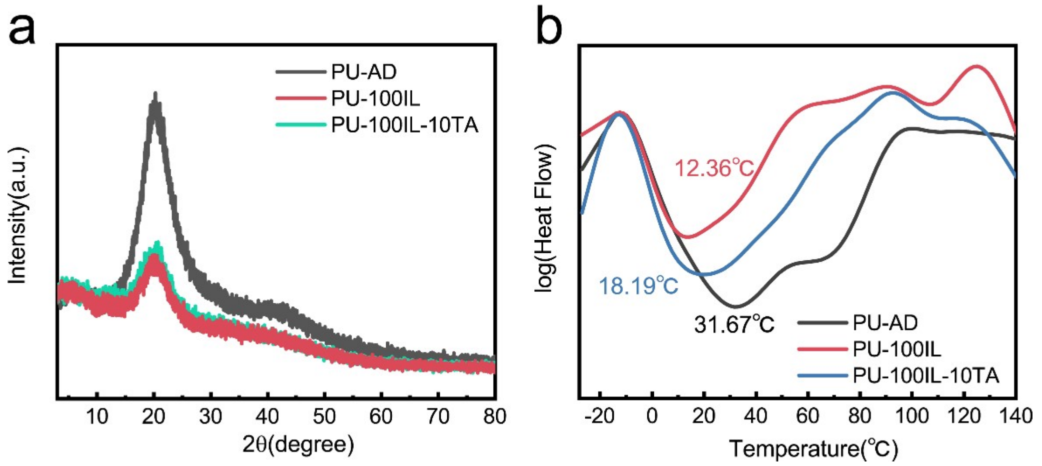

Fig. S14 (a) XRD plots of PU-AD, PU-IL, and PU-IL-TA elastomers. (b) First-order differential plots of differential scanning calorimetry (DSC) curves of PU-AD, PU-100IL, and PU-100IL-10TA.

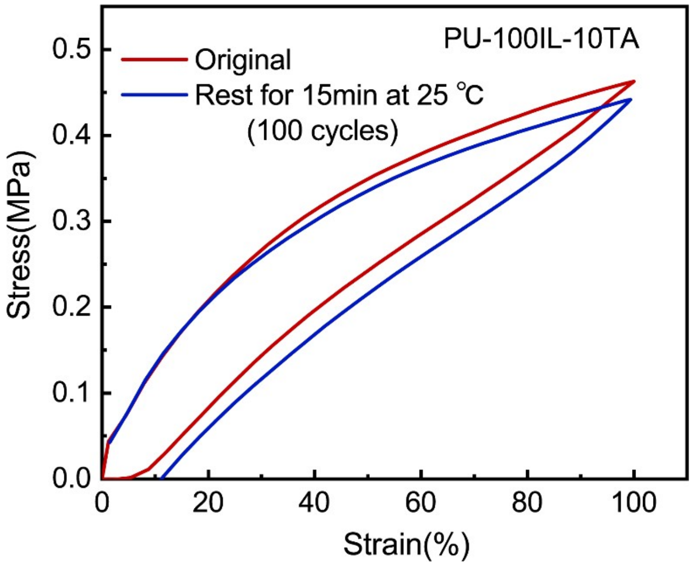

Fig. S15 Cyclic loading–unloading tensile curves of PU-100IL-10TA elastomer waiting for 15 min after 100 cyclic tensile tests at 100% strain.

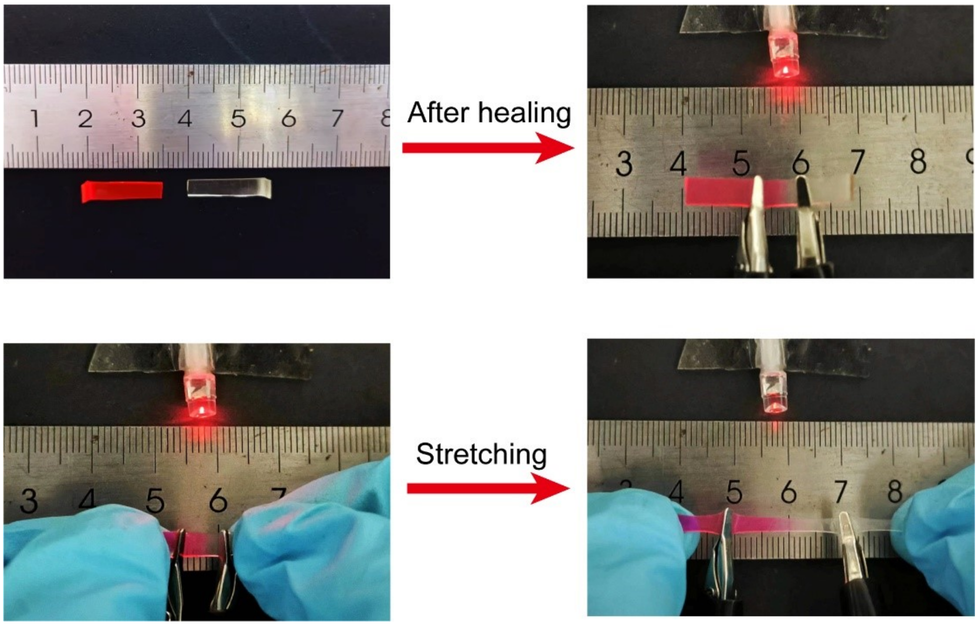

Fig. S16 Digital photographs of the fully healed PU-100IL-10TA elastomer lights up a LED bulb.

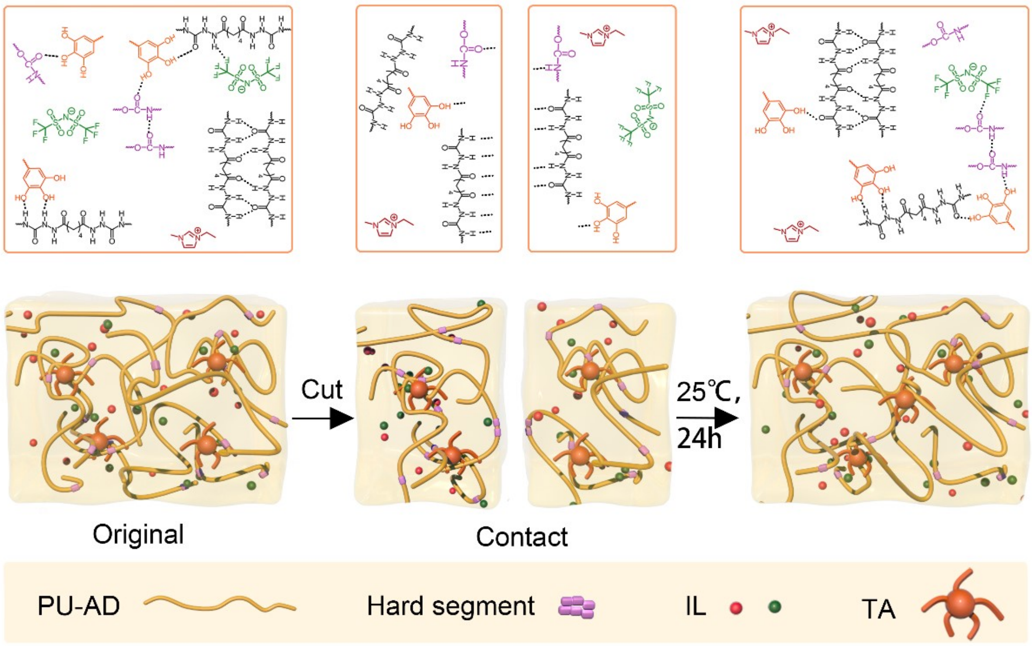

Fig. S17 Schematic illustration of the self-healing process of PU-IL-TA.

Table S3 The weight changes at ~25°C and ~40% RH for PU-AD, PU-IL, and PU-IL-TA elastomers

Elastomers	Initial quality (mg)	Quality after 30 days (mg)	Quality change (%)
PU-AD	288.5	287.0	99.48
PU-IL	286.4	285.9	99.83
PU-IL-TA	287.5	289.6	100.73

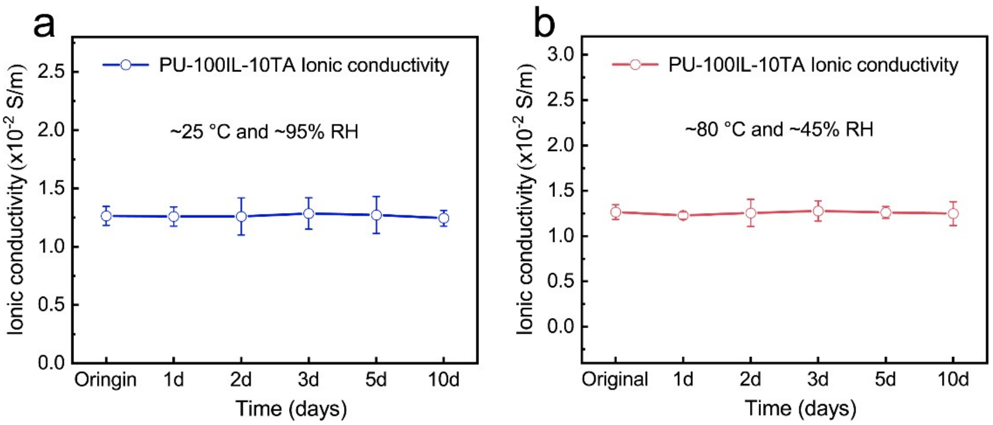

Fig. S18 (a) The ionic conductivity changes of PU-100IL-10TA after being placed at~25 ° C and~95% RH for different days. (b) The ionic conductivity changes of PU-100IL-10TA after being placed at ~80 °C and ~45%RH for different days.

Fig. S19 The IL retention ability of PU-100IL-10TA at a pressure of 2.5 kg. (a) PU-100IL-10TA with a volume of 18mm x 15mm x 1mm and front side of dry A4 paper measuring 35 × 35mm. (b) PU-100IL-10TA was sandwiched between two sheets of A4 paper and placed under a weight of 2.5kg. (c) After 5 minutes, the weights were removed and the A4 paper underneath the PU-100IL-10TA and the reverse side of the 35 × 35 mm A4 paper (the contact surface with the PU-100IL-10TA) were dry.

Movie S1. Twisted PU-100IL-10TA lights up a LED bulb as a stable conductor.

Movie S2. Stretching the notched PU-100IL-10TA.

Movie S3. Fully healed PU-100IL-10TA can easily light up the LED light.

Movie S4 The IL retention ability of PU-100IL-10TA at a pressure of 2.5 kg.