# **Supporting information**

# A Very Mechanically Strong and Stretchable Liquid-Free Double-

# **Network Ionic Conductor**

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### **Experimental Section**

## **Materials**

Choline chloride (ChCl, 98%, Shanghai Macklin Biochemical Co., Ltd), acrylic acid (AA, >99%, Macklin), polyvinylpyrrolidone (PVP,  $M_w$ =220000, K60, Macklin), poly (ethylene glycol) diacrylate (PEG(200)DA, Shanghai Aladdin Reagent), and 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator 2959, ≥98%, Tianjin Jiuri New Materials) were used as received.

#### **Fabrication of AA-ChCl type PDES**

Solid ChCl as the ammonium salt should be dried under vacuum at 65°C for 2 hours. Solid ChCl and AA were mixed in 1:5 mole ratio. Then, the mixture was heated and stirred at 90°C in a closed flask until a homogenous colorless solution was formed. The prepared AA-ChCl type PDES was then kept in a vacuum desiccator with silica gel until further use.

#### **Photopolymerization of PVP-PDES mixture**

Various amount of solid PVP was added into AA-ChCl type PDES and stirred vigorously until a transparent solution was formed at 100°C. Then, 0.1 mol% crosslinkers PEG(200)DA and 0.1 mol% photo-initiator 2959 to comonomers were added into the resulting PVP-PDES mixture. The mixed solution was stirring at room temperature until a homogenous colorless solution was formed. Finally, the precure solutions were fabricated and kept in a vacuum desiccator with silica gel until further use.

For preparing LFDNIC, the precursor solution was injected into two release films coated glassed mold sandwiched with a silicon film, and thickness and shape were determined by silicon film. Then, the reaction was initiated by a UV light source (RW-UVA-Φ200U, Shenzhen Runwing Company, China) with a dominant wavelength of 365 nm within 2 min. The light intensity was 20 mW·cm<sup>-2</sup> measured by the UV radiometer

## Photopolymerization of AA-ChCl type PDES

Liquid-free single-network ionic conductor (LFSNIC) was prepared by in situ photopolymerization of the AA-ChCl type PDES. For preparing LFSNIC, 0.1 mol% crosslinkers PEG(200)DA and 0.1 mol% photo-initiator 2959 to comonomers were added into the resulting AA-ChCl type PDES. Then, the mixed solution was stirring at room temperature until a homogenous colorless solution was formed. The precure solution was injected into two release films coated glassed mold sandwiched with a silicon film, and thickness and shape were determined by silicon film. Finally, the reaction was initiated by a UV light source (RW-UVA- $\Phi$ 200U, Shenzhen Runwing Company, China) with a dominant wavelength of 365 nm within 2 min. The light intensity was 20 mW·cm<sup>-2</sup> measured by the UV radiometer

### Prepare of a strain sensor

The LFDNIC was cut into the size of  $5 \times 1 \times$  thickness cm<sup>3</sup> and copper wires were attached on two ends of the LFDNIC by tapes for electrical signal transmissions. When performing tests, the strain sensor was in series with a Keithlwy DMM7510 source meter to detect the motion of the volunteer.

### Characterization

Differential scanning calorimeter (DSC) was employed a 214 polyma NETZSCH tester. The mixture was placed into aluminum pans and heated at 10°C min<sup>-1</sup> from - 150 to 120°C under a nitrogen atmosphere. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 33 spectrometer. <sup>1</sup>H NMR spectra (400 MHz) were tested using a Bruker spectrometer AVANCE III HD 400. Chloroform (CDCl3) was used as an external reference. The polymeric materials were set to the same condition.

The tensile testing was performed using a tensile machine (INSTRON 5565, 2000 N load cell). The tensile speed was set to 25 mm/min. The samples were cut into  $50 \times 10 \times 0.5$  mm<sup>3</sup>. Dynamic mechanical analysis (DMA) measurements were carried out using Q800 (TA Instruments) equipment working in tensile mode with a

frequency range from 1 to 100 Hz. The surface morphologies of the samples on morphologies were measured by tapping mode atomic force microscopy (AFM, Bruker multimode 8) using tapping MPP-rotated cantilevers with silicon probes (model: RTESP, part MPP-11100-10).

The regular light transmittance was tested by the UV-visible spectrometer (Cary60, Agilent, USA). The wavelength range was 200-800 nm with a speed of 600 nm/min. The electrochemical properties were measured by PGSTAT 302N (Princeton Applied Research) through an AC impedance method. The applied frequency range in the electrical tests was from 1 to  $10^5$  Hz. The ionic conductivity ( $\sigma$ ) was measured employing the electrochemical impedance spectroscopy (EIS) route over a frequency range of 1 to  $10^5$  Hz. The sample was sandwiched between two copper tapes, and the ionic conductivity was calculated by  $\sigma = L/(R \times A)$  where L is the thickness of the elastomer, R is the bulk resistance, and A is the contact area between the two copper tapes. The current signals of sensors were measured in real-time with a Keithley DMM7510 source meter. The optical microscope images of the cutting CE after self-healing were recorded on a polarized optical microscope (OLYMPUS, BX63). Optical images were taken by a Canon EOS 60D camera. The testing conditions were at room temperature 25°C and the humidity was about 35%.

MTT assay was used to evaluate the effect of materials on the cytotoxicity of L929 cells. The L929 cells were first resuscitated and the materials were irradiated with UV light for 30 minutes to sterilize. Then, we collected L929 cells in the log phase, performed cell counting, adjusted cell suspension concentration, and plated the cells to be tested to  $2\times10^4$  cells/well (500 µL of cell suspension per well). Cells and materials were co-cultured for 48h at 37°C with 5% CO<sub>2</sub>. Then, L929 cells were washed with PBS, and 500 µL of MTT solution (0.5 mg×mL<sup>-1</sup>) was added to each well. After continuing the incubation for 4h, the medium and MTT solution were removed. 400 µL of dimethyl sulfoxide was added and it was shaken for 10 min. Subsequently, the liquid was aspirated into a 96-well plate, and 150 µL was added to each well. The absorbance value at 570 nm was measured with an enzyme marker (EPOCH2, Biotek). The cells without any treatment were used as the control group,

and the cell viability of the control group was set at 100%. Therefore, the cell viability of L929 cells in the experimental group = OD experimental group/OD control group×100%. Finally, the sample cells were subjected to live/dead staining experiments and the results were examined with a laser confocal microscope (Leica TCS SP8). Calcein excitation wavelength was chosen to be 488 nm and the excitation wavelength of the dye-DNA complex was 552 nm.

## The details of the Molecular Dynamics Simulation

Molecular Dynamics Simulation was performed to further study the mechanical properties of LFSNIC and LFDNIC materials. The Condensed-Phase Optimized Potentials for Atomistic Simulation Studies II (COMPASSII) force field was used to provide the atomic interactions. The molecules of LFSNIC or LFDNIC were packed in the cell with Monte Carlo method. To equilibrate the model, a equilibrate process was followed under constant pressure and temperature (NPT ensemble) at 298 K for 10 ns. During the simulation, Nosé thermostat was applied in the temperature control. The Ewald summation method was applied to calculate the electrostatic and van der Waals interactions with an accuracy of 10-3 kcal/mol. Constant strain method was used to study the mechanical properties of LFSNIC and LFDNIC.



Fig. S1. Optical photograph of PVP-PDES mixture with different amount of PVP. (a)Clear and transparent PVP-PDES mixture (PVP 0-2 wt.%) without any agglomerates.(b) PVP-PDES mixture (PVP 2.5 wt.%) with some agglomerates.

PDES preparation	PVP (wt.%) to PDES	Photopolymerization for 2 min		
ChCl: AA =1: 5 (mole ratio)	0	Transparent ionic conductor, soft		
	1	Transparent ionic conductor, tough		
	1.5	Transparent ionic conductor, tough		
	2	Transparent ionic conductor, tough		

**Table S1.** The detailed components of diverse PVP-PDES mixture.



Fig. S2. DSC traces of PVP-PDES mixture with different amount of PVP.



Fig. S3. The FTIR spectroscopy of AA, ChCl, PVP, and PVP-PDES mixture,



Fig. S4. <sup>1</sup>H NMR spectrum of PVP-PDES mixture.



Fig. S5. The FTIR spectroscopy of PVP-PDES mixture before (up) and after (down)

photopolymerization.



Fig. S6. The toughness of the LFDNIC with 2 wt.% PVP networks.



Fig. S7. Cyclic stress-strain curves of the LFDNIC with 2 wt.% PVP networks.



Fig. S8. (a) Tensile stress-strain curves of the LFDNIC with 2 wt.% PVP networks

under different tensile speed. (b) Young's modulus of the LFDNIC with 2 wt.% PVP networks under different tensile speed.



**Fig. S9.** Digital image for LFDNIC with 2 wt.% PVP networks that can tolerate puncture.



Fig. S10. (a)Extremely thin LFDNIC (0.09 mm). (b) Its corresponding stress-strain curve.

References	This work	1	2	3	4	5	6	7	8	9	10
Tensile strength (MPa)	71.33	0.09	0.42	0.24	0.15	0.12	0.32	0.3	0.24	0.11	1.5
Strain-at-break (%)	670	150	137	1100	1100	60	1150	450	540	145	1640
Ionic conductivity (S/m)	3*10-4	2*10-2	2*10-2	1*10-7	2*10-3	8*10 <sup>-3</sup>	1*10-6	1*10-2	1*10-2	1*10-3	1*10-3
Biocompatibility	Yes	Yes	No	No	No	No	No	No	No	No	No
Transparency	Yes	Yes	No	Yes	Yes	No	Yes	Yes	No	Yes	Yes
Self- repairability	Yes	Yes	No	No	Yes	Yes	No	Yes	Yes	No	Yes

Table S2. Performance comparison table of this work and other mechanically strong

liquid-free ionic conductors in recent studies.



Fig. S11. The optical and mechanical characterizations for LFSNIC (PVP 0 wt.%)

and LFDNIC (PVP 2 wt.%). (a) Digital image for LFDSNIC. (b) Digital image for LFDNIC. (c) The stress-strain curve of LFSNIC. (d) The stress-strain curve of LFDNIC.



**Fig. S12.** (a) AFM phase image of LFSNIC (PVP 0 wt.%). (b) AFM phase image of LFDNIC (PVP 2 wt.%).



Fig. S13. The result of Molecular Dynamics Simulation. (a) The Molecular Dynamics

Simulation of LFSNIC. (b) The Molecular Dynamics Simulation of LFDNIC.

Simulated mechanical properties	LFSNIC (PVP 0 wt.%)	LFDNIC (PVP 2 wt.%)		
Bulk modulus (Hill)	5.5752 Gpa	5.9489 Gpa		
Shear modulus (Hill)	2.5931 Gpa	3.1078 Gpa		
Young Modulus (x-axis)	7.3587 GPa	8.3729 Gpa		
Young Modulus (y-axis)	7.9793 Gpa	7.6528 Gpa		
Young Modulus (z-axis)	7.4534 Gpa	7.5926 Gpa		

Table S3. Calculated results of Molecular Dynamics Simulation.



Fig. S14. (a) Schematic illustrations of the ChCl attached to PAA network by strong hydrogen bond. (b) color-filled RDG plots (isovalue=0.5) of (a). (c) RDG vs sign( $\lambda 2$ )  $\rho$  for (a) where the sign( $\lambda 2$ )  $\rho$  is ranged from -0.05 to -0.05.



Fig. S15. The transmittance values for a series of LFDNICs with the PVP content

ranging from 0 to 2 wt.%.



Fig. S16. The ionic conductivity of LFDNICs with different PVP content.

Table S4. The conductivity of the PVP-PDES mixture and the corresponding

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LFDNIC.
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The amount of PVP Conductivity (S/m)	0 wt.%	1 wt.%	1.5 wt.%	2 wt.%
PVP-PDES mixture	~0.372	~0.370	~0.360	~0.353
LFDNIC	~0.0018	~0.00062	~0.00037	~0.00031



Fig. S17. The resistance of the LFDNIC with 2 wt.% PVP before cut and after selfhealing.

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