Supporting Information

Low hysteresis zwitterionic supramolecular polymer ion-conductive elastomers with anti-freezing property, high stretchability, and self-adhesion for flexible electronic devices

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Experimental Section

Materials

N, N-Dimethylethylenediamine (98%) was supplied from Macklin Biochemical Technology Co., Ltd. (Shanghai, China), 2-Isocyanatoethyl acrylate (98%) and Dichloromethane (99.9%, extra dry, with molecular sieves,) were purchased from Energy Chemical Co., Ltd. (Shanghai, China). β-propiolactone (98%) was supplied from J&K Scientific Co., Ltd. (Beijing, China). 2-Hydroxy-2-methylpropiophenone (IRGACURE 1173, 97%) was obtained from Sigma-Aldrich (Shanghai, China). Lithium chloride (99%) was purchased from Heowns Biochem Technology Co. Ltd. (Tianjin, China). All other chemicals and solvents were analytical reagents and used as received without further purification.

Synthesis of 2-{3-[2-(Dimethylamino)ethyl]ureido}ethyl Acrylate (DMUEA)

2-{3-[2-(Dimethylamino)ethyl]ureido}ethyl acrylate (DMUEA) was synthesized according to the previously described method[1]. A solution of N, N-dimethylethylenediamine (20.0 mmol, 2.177 ml) in anhydrous dichloromethane (312.0 mmol, 30.0 mL) was added dropwise to a stirred solution of 2-isocyanatoethyl acrylate (20.0 mmol, 5.441 ml) in anhydrous dichloromethane (312.0 mmol, 30 mL) under a nitrogen atmosphere. The solution was stirred at ambient temperature for 2 h under a stream of nitrogen. Then, the mixture solution was concentrated to remove the solvent by the vacuum rotary evaporation, and a colorless oily product was obtained.

Synthesis of carboxybetaine ureido acrylate (CBUIA)

Carboxybetaine ureido acrylate (CBUIA) was synthesized as the followed protocol. Briefly, a certain amount of DMUEA (10.0 mmol) was reacted with β-propiolactoneine (12.6 mmol) in 50 mL of anhydrous acetone at 0 ℃ for 2 h under a nitrogen atmosphere. The white precipitate was washed with anhydrous ether, dried in a vacuum, and stored at 4 ℃. ^{1}H NMR (400MHz, Deuterium Oxide, δ in ppm): 6.42 (dd, J = 17.4, 1.2 Hz, 1H, C*H*H=CH-), 6.19 (dd, J = 17.3, 10.5 Hz, 1H, CH_2=C*H*-), 5.98 (dd, J = 10.5, 1.2 Hz, 1H, CH*H*=CH-), 4.22 (t, J = 5.2 Hz, 2H, -COOC*H*$_2$-), 3.65 - 3.53 (m, 4H, -C*H*$_2$N$^+$(CH$_3$)$_2$C*H*$_2$-), 3.48 - 3.34 (m, 4H, -C*H*$_2$NHCONHC*H*$_2$-), 3.11 (s, 6H, -N$^+$(C*H*$_3$)$_2$-

), 2.67 (t, J = 7.8 Hz, 2H, -CH_2COO$^-$-). ^{13}C NMR (100 MHz, Deuterium Oxide, δ in ppm): 176.22 (-COO$^-$), 168.24 (-COO-), 159.72 (-NHCONH-), 132.50 (CH$_2$=CH-), 127.51 (CH$_2$=CH-), 64.11 (-COOCH$_2$-), 62.64 - 61.88 (-CH$_2$N$^+$(CH$_3$)$_2$$CH_2$-), 50.98 (-N$^+$($CH_3$)$_2$-), 38.72 (-COOCH$_2$$CH_2$-), 33.84 (-$CH_2CH_2N^+$(CH$_3$)$_2$-), 30.77 (-$CH_2COO^-$). The FTIR spectrum shows the characteristic bands of CBUIA: 3253 cm^{-1} corresponds to the N-H stretching vibration, and the peaks at 1670 cm^{-1}, 1611 cm^{-1} and 1270 cm^{-1} are ascribed to C=O stretching vibration (amide I mode), N-H bending vibration (amide II mode) and C-N stretching vibration (amide III mode). In addition, there is a C=C stretching vibration mixed at 1670 cm^{-1}.

Preparation of PCBUIA ICEs

A certain amount of CBUIA was dissolved in 1 ml deionized water or LiCl aqueous solution, and then the photoinitiator IRGACURE 1173 (1 wt%) was added into the above solution. The mixture solution was poured into a customized mold with the dimensions of 40×60×1 mm^3, which was fabricated from PET release films and glass plates spaced by a silicone frame to control gel thickness. Finally, the mold was placed in a UV cross-linking box (XL-1000 UV Crosslinker, Spectronics Corporation, NY, USA) and irradiated for one hour to obtain PCBUIA gels. Placed the prepared gels in a constant temperature and humidity box (the relative humidity and temperature were set as 55% and 35 ℃, respectively) for 7 days to allow the water to evaporate to obtain the PCBUIA elastomers. For simplicity, the obtained elastomers are denoted as PCBUIA-X or PCBUIA-LiCl-X-Y, where X and Y represent the feeding concentrations of CBUIA in mol/L and LiCl in wt%, respectively.

Characterizations

The chemical structures of CBUIA were characterized by a nuclear magnetic resonance (NMR) spectrometer (AVANCE III, 400 MHz, Bruker, Japan) by using deuterium oxide as the solvent and a Fourier transform infrared (FTIR) spectrometer (Nicolet™ iS20, Thermo Fisher, USA). The variable-temperature ^{1}H NMR spectra of PCBUIA were recorded with a solid-state NMR spectrometer (JNM ECZ600R, JEOL, Japan) at 50, 60, 70, 80 and 90 ℃, respectively. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of PCBUIA elastomer were recorded on a Fourier

transform spectrometer (Nicolet™ iS50, Thermo Fisher, USA) to analyze the intermolecular hydrogen-bonding interactions on the side chains of PCBUIA. The sample was vacuum dried at 80 °C for 6 hours before testing and the spectra were recorded with a scanning range of 4000-600 cm^{-1}. The ordered structures in PCBUIA-LiCl elastomers were characterized by bench X-ray diffraction (D8 Advanced, Bruker, Germany). The radiation source was Cu Kα, with a wavelength of 0.154 nm, and the set test parameters were as follows: voltage 40 kV, current 40 mA, scan range 2θ from 5° to 45° at a scanning rate of 4° min^{-1}. The micromorphology of PCBUIA-LiCl-4-20 elastomer was analyzed by a small angle X-ray scattering (SAXS, Xeuss 3.0, France). The effective scattering vector range q was from 0.008 to 0.262 Å^{-1} (1 Å^{-1} = 10nm^{-1}, q

$= \dfrac{4\pi sin\theta}{\lambda}$, where 2θ is the scattering angle and λ is the wavelength).

The transparency of PCBUIA-LiCl ICEs was evaluated on a UV-vis spectrophotometer (GENESYS 180UV, Thermo Scientific, USA) with quick mode from 400 to 800 nm. The thermal properties of PCBUIA-LiCl ICEs were assessed by differential scanning calorimetry (DSC, Q2000, TA Instrument, USA) according to the following protocol: cooling from 25 to -80 °C at 10 °C/min, and reheating from -80 °C to 25 °C at 10 °C/min. The samples were vacuum-dried at 80 °C for 6 hours before testing. Rheological behaviors of the PCBUIA-LiCl-4-20 elastomer were analyzed using a rheometer (MCR302, Anton Paar, Austria) equipped with a parallel plate (diameter, 25 mm) through a small-amplitude oscillatory shear mode. Thermogravimetric analysis (TGA) tests of PCBUIA-LiCl ICEs were carried out using a thermogravimetric analyzer (STA 200, HITACHI, Japan). The atmosphere was nitrogen, the heating rate was 10 °C/min, and the test temperature range was from room temperature to 800 °C.

Measurement of mechanical properties

The mechanical performances of PCBUIA-LiCl elastomers were evaluated by an electronic universal testing machine (Legend 2344, Instron, USA) equipped with a 500 N sensor at room temperature. For tensile tests, PCBUIA-LiCl elastomers were prepared into dumbbell shape samples 35×2.1×1 mm^3 according to ASTM standards

and all tests were performed at a constant rate of 50 mm/min. For the compression test, cylindrical specimens with a diameter of 8 mm were tested at a constant rate of 10 mm min^{-1}. For the load-unload tensile tests, the dumbbell-shaped samples were first stretched to a predetermined strain at a stretching rate of 50 mm/min, and then immediately returned to the initial state at the same speed. For the load-unload compression tests, cylindrical specimens were performed at a speed of 10 mm min^{-1} under a strain of 80%. Young's modulus and compressive modulus were calculated from the initial slope of the stress-strain curves with a strain from 10 to 20%, toughness was defined as the area under the stress-strain curve, and the dissipated energy was estimated by integrating the area between the loading-unloading curves. The hysteresis (h) is calculated as follow:

$$h = 1 - \frac{W_{unloading}}{W_{loading}}$$

(1)

where $W_{loading}$ and $W_{unloading}$ are the areas under the loading and unloading stress-strain curves, respectively[2].

All mechanical tests were repeated at least three times, and the results were expressed as the result ± standard deviation. To further evaluate the mechanical properties of PCBUIA-LiCl elastomers under the low temperature, dumbbell shape samples were placed at -20 °C for half an hour in advance and then tested by computerized electronic universal testing machine at -20 °C.

Computer simulation calculations

For the calculation of CBUIA and water, several water molecules were manually placed around CBUIA, and the analytical linearized Poisson-Boltzmann (ALPB) model was used to explain the solvation effect of water. The next step is to optimize the filtered structure through DFT. All DFT calculations were performed using Gaussian 16 software and adopted the B3LYP functional. The def2-SVP basis set was used for geometry optimization and frequency calculations to determine the optimal geometry for each compound. For single-point energy calculations, we used a larger ma-def2-TZVPP basis set[3]. Furthermore, Weak interactions were corrected by DFT-D3 dispersion correction with BJ damping[4] to improve calculation accuracy, the SMD

implicit solvation model[5] was utilized to account for solvation effects, and Multiwfn software[6] was used for electron density analysis of the Bond critical point. Calculate the hydrogen bond energy through the following fitting formula[7]:

$$\text{Neutral H-bonds: } \Delta E \approx - 223.08 \times \rho(r_{BCP}) + 0.7423 \tag{2}$$

$$\text{Charged H-bonds: } \Delta E \approx - 332.34 \times \rho(r_{BCP}) - 1.0661 \tag{3}$$

Adhesion test

The adhesive strength of PCBUIA-LiCl ICEs was measured by the lap shear test. Before adhesion, the substrates were cleaned with deionized water and ethanol, and completely dried at room temperature. Briefly, a rectangular elastomer $10 \times 10 \times 1$ mm^3 is attached between the surfaces of two substrates; then the bonded substrates exert a certain force to prepare adhesion test samples. Next, the adhesion strength, determined by dividing the maximum tension of joint failure by the overlap area, was measured on a tensile machine at a tensile speed of 50 mm/min. When measuring low-temperature adhesion strength, place the test samples at -20 °C for half an hour before testing. All adhesion tests were repeated at least three times, and the results were expressed as the result ± standard deviation.

Electrical measurements

The ionic conductivity of PCBUIA ICEs with different concentrations of LiCl was measured by alternating current impedance. The ICEs were sandwiched between two stainless steel electrodes, and the alternating-current impedance was performed on an electrochemical workstation (CHI660E, CH Instruments, USA) with a frequency range of 1 MHz to 0.01 Hz and an amplitude of 10 mV. The conductivity was calculated using the following equation:

$$\sigma = \frac{L}{(R \times A)} \tag{4}$$

where L represents the distance between the positive and negative electrodes, and R and A represent the bulk resistance and cross-sectional area of the elastomer samples, respectively.

Sensing measurements

The ICE strips $30\times10\times2$ mm^3 were loaded onto an electronic universal testing machine (Legend 2344, Instron, USA) for tensile testing. The two ends were connected to a precision impedance analyzer (TH2839A, Tonghui, China) through wires to record the changes in electrical resistance, and the relative resistance change was calculated by the following formula:

$$\frac{\Delta R}{R_0} = \frac{(R - R_0)}{R_0} \times 100\%$$

(5)

where R and R_0 were the resistances when the strain was applied and no strain was applied, respectively.

The gauge factor (GF), an important indicator of sensor sensitivity, was calculated by the following equation:

$$GF = \frac{\dfrac{(R - R_0)}{R_0}}{\varepsilon}$$

(6)

Here, R and R_0 were the resistances when the strain was applied and no strain was applied, respectively. ε is the strain exerted on the elastomers.

To further evaluate the sensing performance of ICEs for detecting human motion, the elastomer was directly attached to the human body, and the resistance changes were recorded by a Precision Impedance Analyzer.

Fabrication and Characterization of PCBUIA ICEs-based Triboelectric Nanogenerator (TENG)

Fabrication of the Polydimethylsiloxane (PDMS) films: First, the base resin was mixed with the curing agent at a weight ratio of 10: 1 to form a PDMS solution. Then, the Petri dish was placed on the heating table at 50 °C and baked for 15 minutes. After that, the glass sheet was spin-coated three times using a spin coater at 500 r/min. The coated glass sheet was then dried in a drying oven at 80°C for 2 hours. Finally, the PDMS film was cut into a size of 3×3 cm^2.

Fabrication of the PCBUIA ICEs-based TENG: The ionic conductive elastomer film (2×2 cm^2) with a thickness of 1 mm was used as electrode material, and two PDMS films were used as triboelectrically charged layers. A single electrode mode TENG was assembled by sandwiching the ICE film between the PDMS films, and a copper foil attached to the surface of the elastomer.

Fabrication of wireless finger motion monitoring system: The wireless motion monitoring system was integrated by two wearable PCBUIA ICE-based TENGs on the index and middle finger, a multi-channel signal acquisition and processing module, a wireless signal transmission module, a cloud computing platform, and WeChat mini program.

Supporting Figures
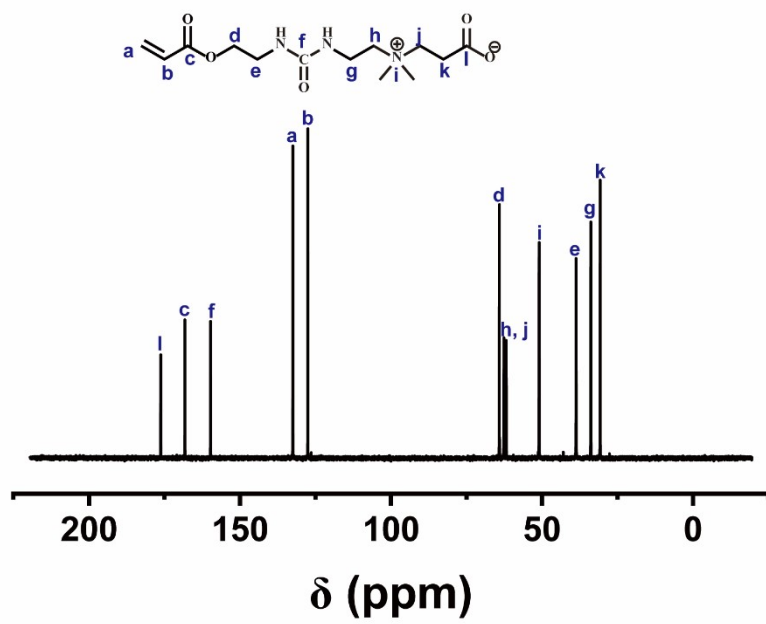
Fig. S1 ^{13}C NMR spectrum of CBUIA in D$_2$O.
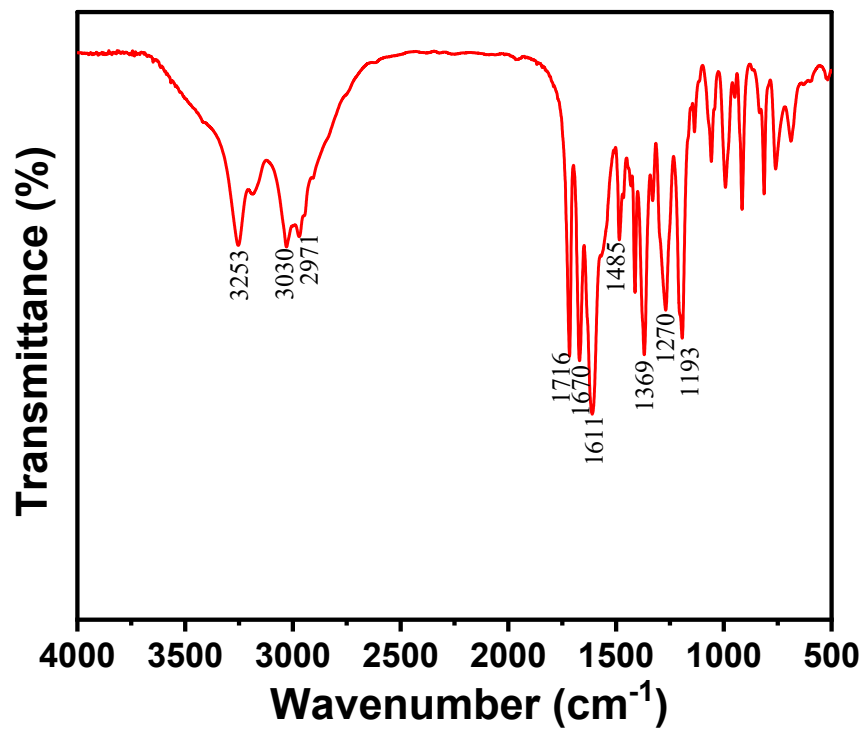
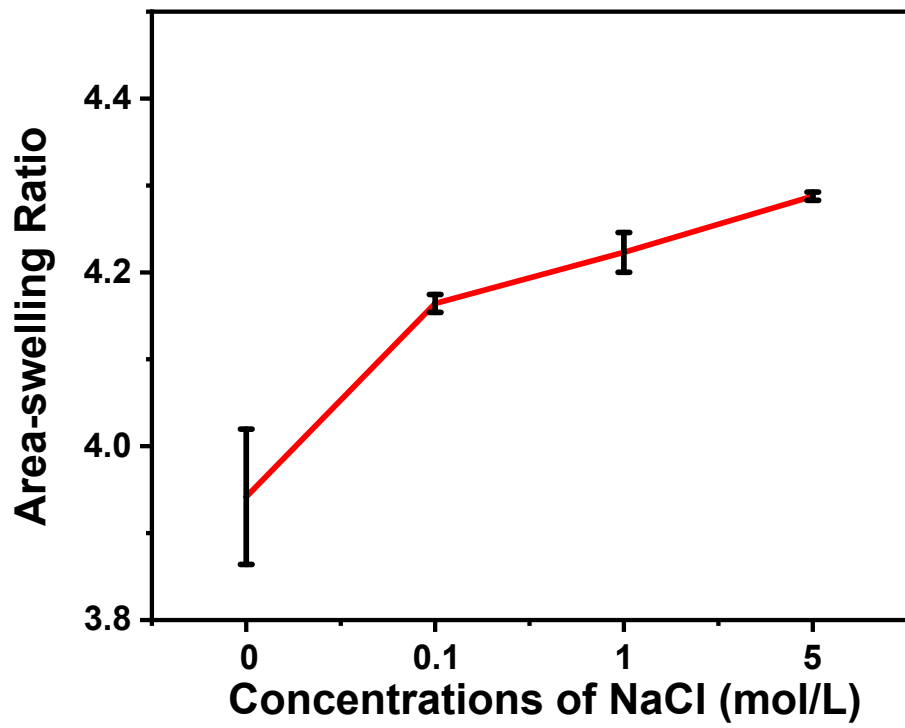Fig. S2. FTIR spectrum of PCBUIA elastomer.

Fig. S3. Area-swelling ratios of PCBUIA hydrogels immersed in different concentrations of

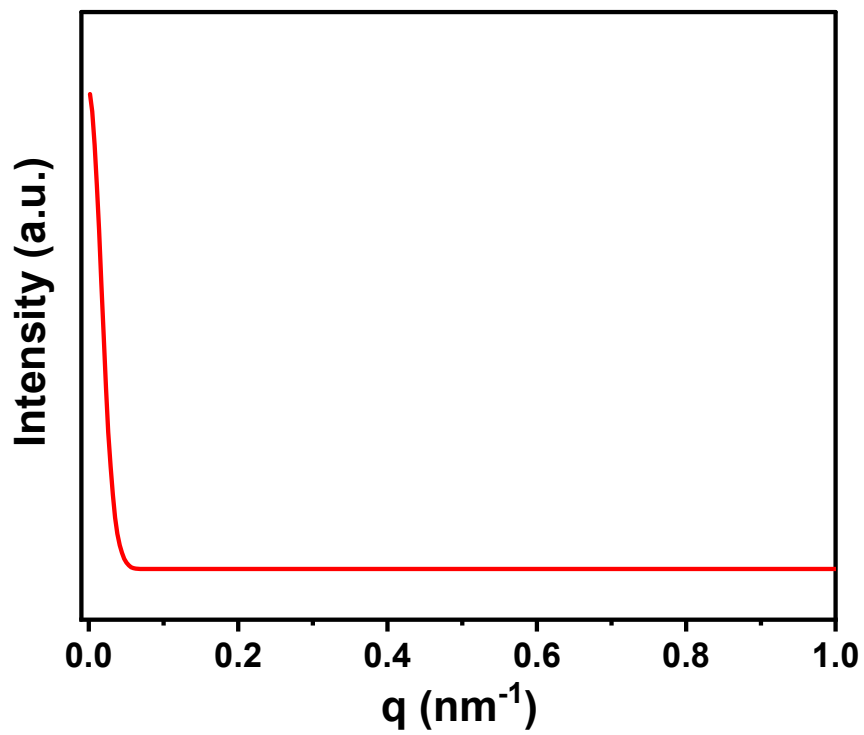sodium chloride solution for 24 h.
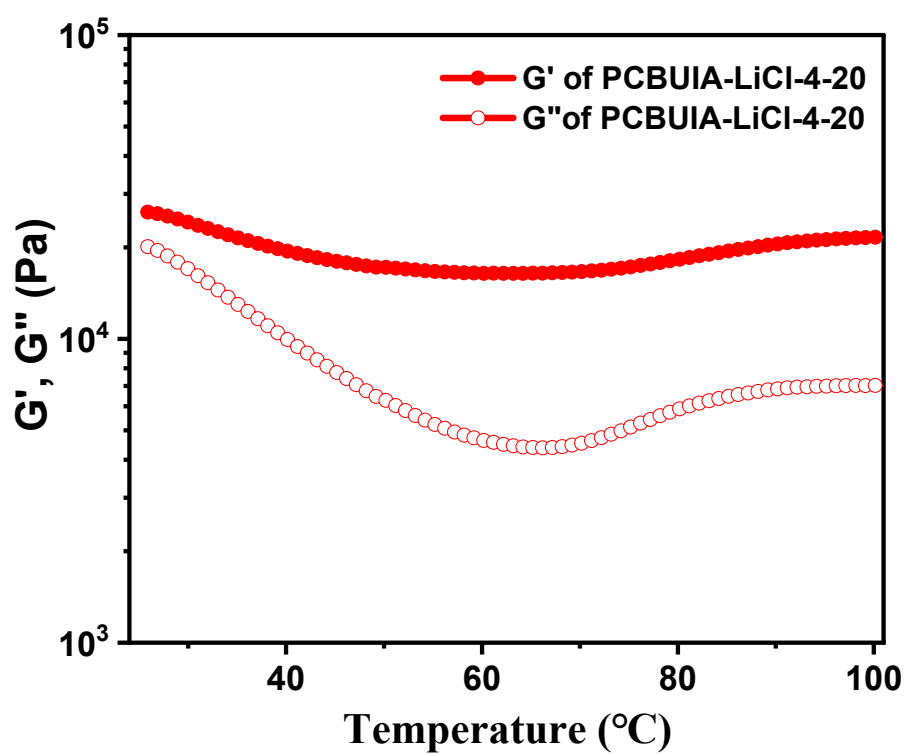
Fig. S4. SAXS profile of PCBUIA-LiCl-4-20 elastomer.

Fig. S5. Temperature-sweep curves of PCBUIA-LiCl-4-20 elastomer in small amplitude

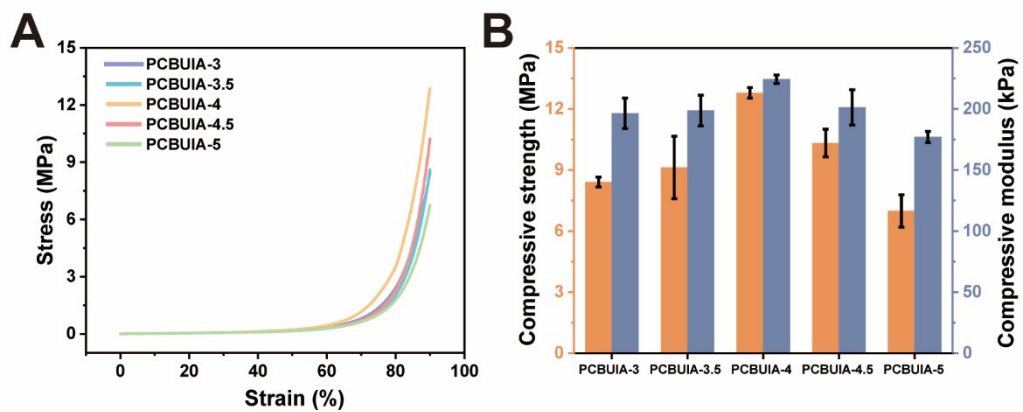oscillatory mode. Strain amplitude, 0.1%; frequency, 1 Hz.

Fig. S6. (A) Compressive stress-strain curves and (B) corresponding compressive strength and compress modulus of PCBUIA-X elastomers.
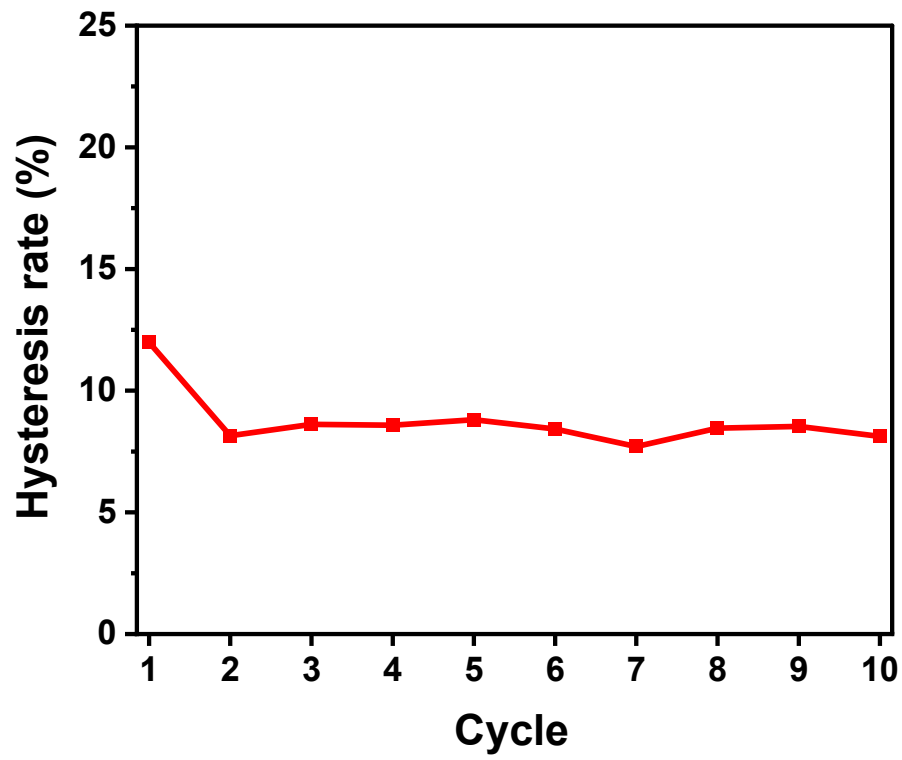
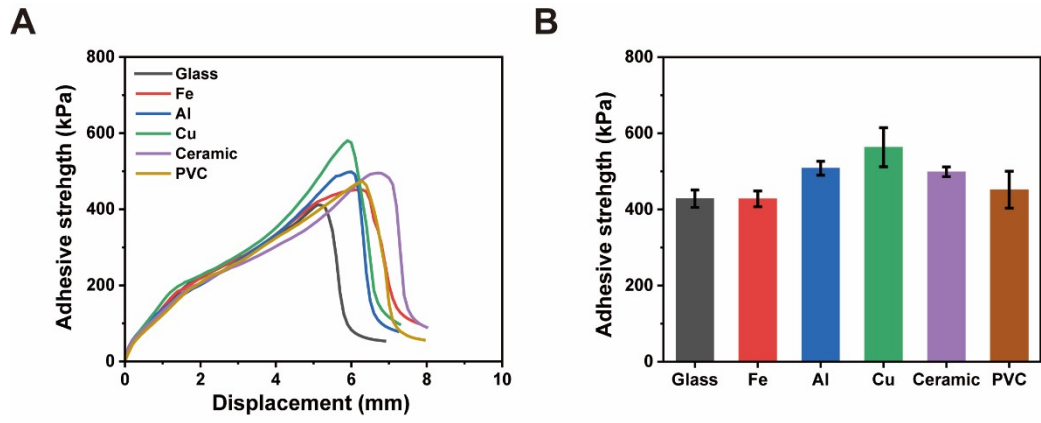Fig. S7. Hysteresis rate of different cycle times at 300% strain.

Fig. S8. (A) Lap-shear curves and (B) corresponding adhesive strengths of PCBUIA-4 elastomers to different substrates. Lap-shear tests are performed at room temperature with a stretch rate of 50 mm/min.
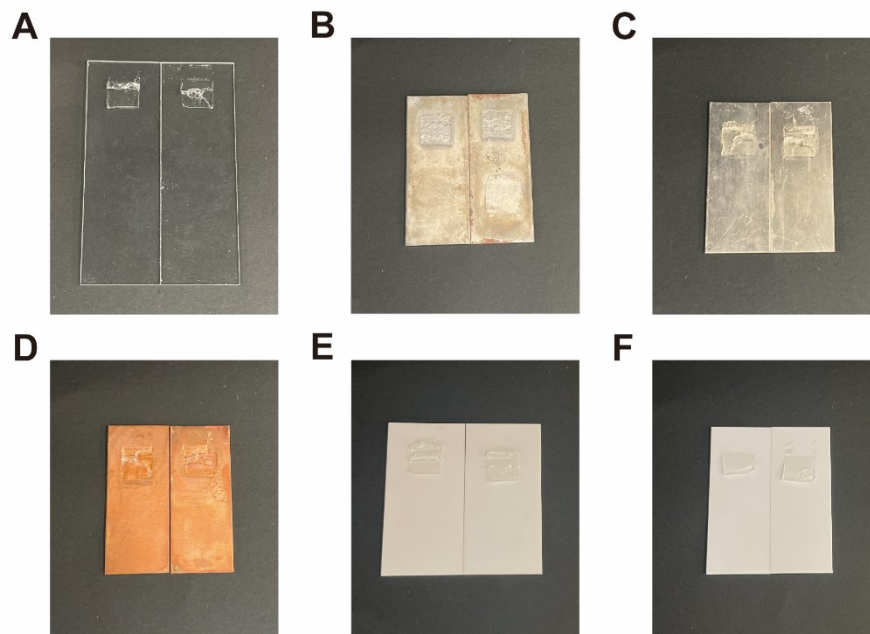
Fig. S9. Digital photos of the fractured surfaces of PCBUIA-LiCl-4-20 elastomers after lap-shear tests. (A) Glass, (B)Ferrum, (C) aluminum, (D) copper, (E) Ceramic, and (F) PVC.
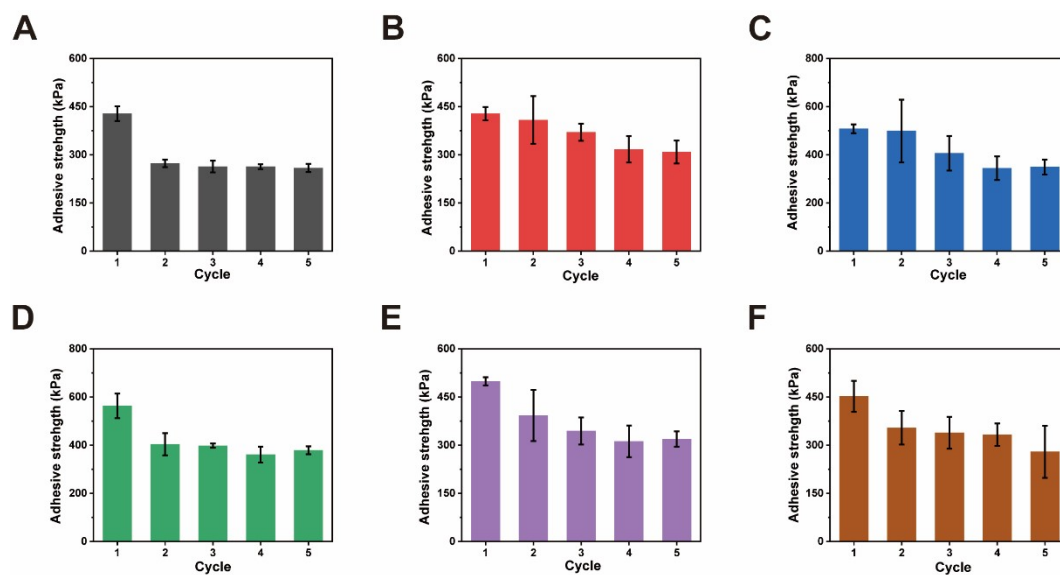
Fig. S10. Repeated adhesion properties of the PCBUIA-4 elastomers to different substrates. (A) Glass, (B)Ferrum, (C) aluminum, (D) copper, (E) Ceramic, and (F) PVC. Lap-shear tests are performed at room temperature with a stretch rate of 50 mm/min.
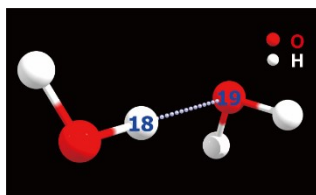
Fig. S11. Conformation of H_2O-H_2O.

Supporting Tables

Table S1. Selected bonding lengths (Å) and bonding energy (kcal/mol) for CBUIA-H_2O and H_2O-H_2O.

Model	Hydrogen bonds	Bonding Length (Å)	Bonding Energy (kcal/mol)
CBUIA-H_2O	H15-O14	1.74623	-15.24
	H2-O1	1.64832	-18.20
	H7-O3	1.97324	-4.79
	H19-O8	1.71448	-8.93
	H16-O17	2.13153	-2.86
	H13-O12	1.84969	-6.31
H_2O-H_2O	H18-O19	1.81224	-7.33

Composition	Transparency	Antifreeze	Adhesion	Low hysteresis	Water retention	Ref
PCBUIA/LiCl	transparent	-63.14 ℃	895.32 kPa	12.03%	30 days	**This work**
SA/TA/PAM	Opaque	-	46 kPa	-	-	[8]
P(BMA-co-MEA)/LiTFSI	transparent	-	-	42%	-	[9]
P(AA-co-HEMA-co-SBMA)	transparent	-21.2 ℃	9.5 kPa	-	-	[10]
PDA-clay-PSBMA	Opaque	-	94.3 kPa	-	-	[11]
PAA/BT/PDA	Opaque	-15	1.8 kPa	-	6 days	[12]
Tara-Fe^{3+}-PAA-CSMA	transparent	-	16 kPa	-	-	[13]
RSF/$CaCl_2$/HRP	transparent	-30 ℃	-	-	10 days	[14]
PAOAM-PDO	transparent	-24 ℃	81.6 kPa	-	10 days	[15]
HPMC-g-P(AM/AA/C18)−$ZnCl_2$	Opaque	-20 ℃	5.5 kPa	-	-	[16]

Table S2. Summary of performance results of reported sensors.

Notes: "-"means Not mentioned.

Supporting Movies

Movie S1: PCBUIA-LiCl-4-20 elastomer can easily and immediately return to its original shape after 50g of weight is removed.

Movie S2: PCBUIA-LiCl-4-20 elastomer could easily and immediately return to its original shape after removing the applied external force of compression.

Movie S3: PCBUIA-LiCl-4-20 elastomer displayed admirable adhesion to the back of the hand, and could be peeled off the human skin without any residue.

Movie S4: Demonstration of PCBUIA ICE-based TENG self-powered finger motion sensing system.

Supporting References

1 Z. Wang, C. Xiang, X. Yao, P. Le Floch, J. Mendez, Z. Suo, PNAS, 2019, 116, 5967-5972.

2 Y. Sun, Y. Ding, W. Zhou, X. Wang, C. Tan, Y. Matsumura, B. Ochiai, Q. Chu, *ACS Omega*, 2021, **6**, 28004-28011.

3 J. J. Zheng, X. F. Xu, D. G. Truhlar, *Theor. Chem. Acc.*, 2011, **128**, 295-305.

4 S. Grimme, S. Ehrlich, L. Goerigk, *J Comput Chem*, 2011, **32**, 1456-1465.

5 A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J Phys Chem B*, 2009, **113**, 6378-6396.

6 T. Lu, F. Chen, *J Comput Chem*, 2012, **33**, 580-592.

7 S. Emamian, T. Lu, H. Kruse, H. Emamian, *J Comput Chem*, 2019, **40**, 2868-2881.

8 H. Qiao, P. Qi, X. Zhang, L. Wang, Y. Tan, Z. Luan, Y. Xia, Y. Li, K. Sui, *ACS Appl Mater Interfaces*, 2019, **11**, 7755-7763.

9 C. Luo, Y. T. Chen, Z. K. Huang, M. Fu, W. B. Ou, T. R. Huang, K. Yue, *Adv. Funct. Mater.*, 2023, **33**, 2304486.

10 Y. Zhang, H. Liu, P. Wang, Y. Y. Yu, M. Zhou, B. Xu, L. Cui, Q. Wang, *Eur. Polym. J.*, 2023, **186**, 111824.

11 X. J. Pei, H. Zhang, Y. Zhou, L. J. Zhou, J. Fu, Mater. Horiz., 2020, **7**, 1872-1882.

12 L. Wu, L. W. Li, M. J. Qu, H. Wang, Y. Z. Bin, *ACS Appl. Polym. Mater.*, 2020, **2**, 3094-3106.

13 J. C. Liu, S. Bao, Q. J. Ling, X. Fan, H. B. Gu, *Polymer*, 2022, **240**, 124513.

14 B. H. Zhao, Q. Y. Chen, G. H. Da, J. R. Yao, Z. Z. Shao, X. Chen, *J. Mater. Chem. C*, 2021, **9**, 8955-8965.

15 L. Zhao, Q. Ling, X. Fan, H. Gu, *ACS Appl Mater Interfaces*, 2023, **15**, 40975-40990.

16 X. L. Zhao, H. X. Wang, J. N. Luo, G. L. Ren, J. F. Wang, Y. Chen, P. X. Jia, *ACS Appl. Polym. Mater.*, 2022, **4**, 1784-1793.