

Phase-locked constructing dynamic supramolecular ionic conductive elastomers with superior toughness, autonomous self-healing and recyclability

Jing Chen

Xi'an jiaotong university

Yiyang Gao

Xi'an Jiaotong University

Lei Shi

School of Materials, Sun Yat-sen University

Wei Yu

Xi'an jiaotong university.

Zongjie Sun

School of Chemistry, Xi'an Jiaotong University

Shuang Liu

StateKey Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences

Heng Mao

Xi'an jiaotong university.

Dongyang Zhang

School of Chemistry, Xi'an Jiaotong University

Quan Chen

Changchun Institute of Applied Chemistry <https://orcid.org/0000-0002-7771-5050>

Demei Yu

School of Chemistry, Xi'an Jiaotong University

Shujiang Ding (✉ dingsj@mail.xjtu.edu.cn)

School of Chemistry, Xi'an Jiaotong University

Article

Keywords:

Posted Date: December 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1131433/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Stretchable ionic conductors are considerable to be the most attractive candidate for next-generation flexible ionotronic devices. Nevertheless, high ionic conductivity, excellent mechanical properties, good self-healing capacity and recyclability are necessary but can be rarely satisfied in one material. Herein, we demonstrate a novel ionic conductor design, dynamic supramolecular ionic conductive elastomers (DSICE), via “phase-locked” strategy, wherein “locking soft phase” polyether backbone conducts lithium-ion (Li^+) transport and the combination of dynamic disulfide metathesis and stronger supramolecular quadruple hydrogen bonds in the hard domains contributes to the self-healing capacity and mechanical versatility. The dual-phase design performs its own functions and the conflict among ionic conductivity, self-healing capability, and mechanical compatibility can be thus defeated. The well-designed DSICE exhibits high ionic conductivity ($3.77 \times 10^{-3} \text{ S m}^{-1}$ at 30°C), high transparency (92.3%), superior stretchability (2615.17% elongation), strength (27.83 MPa) and toughness (164.36 MJ m^{-3}), excellent self-healing capability ($\sim 99\%$ at room temperature) and favorable recyclability. This work provides a new strategy for designing the advanced ionic conductors and offers promise for flexible ionotronic devices or solid-state batteries.

Main

Inspired biologically, stretchable ionic conductors with the ion-conducting nature and sensory functions have been widely applied into soft ionotronic devices¹⁻⁶, such as stretchable touch panels^{7,8}, actuators and sensors^{9,10}, ionotronic diodes and transistors¹¹, triboelectric nanogenerators¹²⁻¹⁴ and others. The majority of current ionic conductors, such as hydrogels and ionogels^{2,14-20}, come in many flavors with diverse capabilities and limitations. In these systems, large amount of liquid provides free ions mobile environment and covalent crosslinked network contributes to the mechanical strength. However, the presence of liquid leads to poor thermal and electrochemical stability and mechanical deleterious effect²¹⁻²³, covalent crosslinked network results in the irreversibility of the polymer structure^{24,25}, thereby generating the canonical conflict between ionic conductivity, self-healing capability and mechanical performance, and becoming unfavorable for the flexible and wearable ionotronic devices. Many researchers have committed to breaking the aforementioned trade-off and constructing versatile ionic conductive elastomers²⁶⁻²⁹. Typical strategy is designing novel polymer molecular structures.

Materials properties depend on its molecular structure. High mechanical strength is mainly derived from the frozen covalent crosslinked network, in which the chain segmental motion is restricted. However, high stretchability requires fewer crosslinking sites and more free mobile chain segments. Employment of supramolecular non-covalent chemistries³⁰⁻³² or dynamic covalent bonds³³⁻³⁵ as reversible crosslinks and sacrificial bonds endow the polymer structure with the reversibility feature, providing materials with self-healing capacity and recyclability to extend their service life and improve their reliability and durability^{36,37}. Ions transport in the liquid-free polymer systems relies on the polymer polarity and the segmental motions^{38,39}. These different properties originating from different molecular mechanism are

generally mutually exclusive⁴⁰⁻⁴³. Therefore, it is a long-standing challenge to achieve the combination of high strength and high toughness with self-healing capacity and recyclability into a given synthetic ionic conductive elastomers. Most of the as-reported liquid-free ionic conductive elastomers with mechanical versatility and self-healability were obtained by introducing supramolecular hydrogen-bonding into the designed ionic conductive polymer networks^{28,40-46}. Jia et al. recently synthesized a novel liquid-free ionic conductive elastomer (ICE) hosting lithium (Li^+) cations and associated anions via lithium bonds and hydrogen bonds, which features high strength and toughness, self-healing behavior, quick self-recovery, 3D-printability, as well as thermal stability and optical transparency²⁹. However, the structural characteristic makes this novel ICE unrecyclable and difficult to repair macroscopic damages.

The compatibility among the ionic conductivity, self-healing and mechanical properties in the polymer electrolytes has been addressed through several polymer engineering strategies. The most eminent strategy is based on the hard-soft dual-phase block copolymer, in which hard block (polystyrene, PS) contributed to mechanical strength and the soft block (polyethylene oxide, PEO) was responsible for ion transport⁴⁷⁻⁴⁹. In addition, nanoscale-phase separation strategy has been proposed to avoid the occurrence of contradictory properties⁵⁰. Guan et al. proposed a phase-separated structure to settle the conflict between mechanical and self-healing ability, in which the polystyrene provided the increasing modulus, and the terminated amide groups were in charge of self-healing mission⁵¹. Then, Bao et al. introduced the supramolecular design into a polyurethane (PU) network to overcome the conflict between mechanical robustness and ionic conductivity⁵². Moreover, many design strategies including the combination of supramolecular H-bonding interactions and metal ligand bonds, phase separation, and dynamic hard domains were also achieved⁵³⁻⁵⁶.

In this work, inspired by polymer electrolytes for solid-state lithium-ion batteries, and combining with dynamic supramolecular engineering, we design a novel dynamic supramolecular ionic conductive elastomers (DSICE) via “phase-locked” strategy, wherein “locking soft phase” polyether backbone conducts lithium-ion (Li^+) transport and the synergistic interaction of dynamic disulfide metathesis and stronger supramolecular quadruple hydrogen bonds in the hard phase contributes to the self-healing capacity and mechanical versatility. The well-designed DSICE possesses good ionic conductivity, high optical transparency, superior mechanical robustness and toughness, excellent autonomous self-healing ability and favorable recyclability. With these desirable traits, we have demonstrated its application for a flexible ionic conductive substrate and a stretchable touch sensor.

Molecular Design and Preparation of DSICE

Thermoplastic polyurethane (TPU) system with distinct two-phase morphology is well known to possess fine-tuned structures and microphase separation of soft segments and hard segments. In view of this specific structure of TPU combing with Li-ion [transport mechanism](#), the soft phase polyether was employed to associate/dissociate Li^+ and the counterparts and transport ions, while the dynamic disulfide metathesis (S-S) and stronger supramolecular quadruple hydrogen bonds (H-bonds) in the hard

phase domains was used to regulating the self-healing capacity and mechanical properties. In the case of keeping the structure and function of the soft phase fixed and regulating that of the hard phase, we define this as “soft phase-locked” strategy, as shown in Fig. 1. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) with large anion group, high ionic conductivity, good solubility, and electrochemical and thermal stability was chosen as conductive lithium salt. The soft phase was chosen as polytetramethylene ether glycol (PTMEG, $M_n = 2000 \text{ g mol}^{-1}$), in which the loosely coordinating O-Li⁺ interaction can contribute to higher ion conductivity^{57,58}. The hard phase featuring dynamic disulfide metathesis (S-S) and strong supramolecular quadruple hydrogen bonding (H-bonds) was chosen as aliphatic bis(2-hydroxyethyl) disulfide (HEDS) and cyclic 2-ureido-4-pyrimidinone (UPy), wherein HEDS mainly contribute to the self-healing capability, and UPy is used for mechanical enhancement. Multiple dynamic bonds including disulfide metathesis (S-S), cooperative crosslinking H-bonds (UPy-UPy) and anti-cooperative crosslinking H-bonds (urethane-urethane, urea-urea, or urea-urethane) spontaneously form a dynamic supramolecular polymer network.

First, transparent and colorless dynamic supramolecular elastomers (DSE) were successfully synthesized via condensation polymerization. To systematically study the synergistic interaction of dynamic disulfide metathesis (HEDS) and supramolecular crosslinking quadruple H-bonds (UPy) on the DSE properties, a series of DSEs, which was denoted as DSE-0, DSE-1, DSE-2, DSE-3, was synthesized through increasing the content of UPy from 0% to 30% (mol %). The preparation procedure is shown in Fig. S1. PTMEG-based prepolymer was first synthesized with two equivalents of hydrogenated 4,4'-methylenediphenyl diisocyanate (HMDI) and a certain amount of dibutyltin dilaurate (DBTDL) as a catalyst, followed by chain extension using bis(2-hydroxyethyl) disulfide (HEDS) and 2-ureido-4-pyrimidinone (UPy) in a given ratio. Compared to hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), HMDI with the alicyclic isocyanates has large steric hinderance preventing crystallization, resulting in completely amorphous transparent colorless materials. Then, a certain amount of LiTFSI was introduced into the optimal DSE polymers for fabricating dynamic supramolecular ionic conductive elastomers (denoted as DSICE).

Characterization of DSE

Fig. 1a showed the schematic diagram of the as-synthesized DSE macromolecules. ¹H NMR proved the successful [synthesis](#) of DSE, as indicated by the characteristic peaks of PTMEG, HMDI, HEDS and UPy segments in polymeric backbones (Fig. S2). Fourier transform infrared (FTIR) spectra and Raman spectra further confirmed the successful [preparation](#) of DSE. The N=C=O disappearance of the peaks at 2260 cm^{-1} and the increasing peaks at $\sim 1660 \text{ cm}^{-1}$ and $\sim 1695 \text{ cm}^{-1}$ associated with H-bonded C=O in urea and urethane in the FTIR spectra (Fig. S3) indicate that the diisocyanate monomers were completely converted into urethane or urea moieties and the increasing amount of UPy in the DSE polymers. The peaks at 510 cm^{-1} and 640 cm^{-1} in the Raman spectra (Fig. S4) belong to the $\nu(\text{S-S})$ and $\nu(\text{C-S})$, respectively, suggesting that disulfide bonds have been successfully introduced into the DSE systems.

The molecular weight and polymer dispersity index (PDI) of all DSE samples were presented in Fig. S5 and Table S1.

The microstructure of DSE samples was systematically investigated. Fig. 2a presented small angle X-ray scattering (SAXS) profile plots of DSE specimens. It can be observed that the single broad peak intensity increases with the increasing UPy motifs, indicating more prominent accumulation of the hard segments and the increasing microphase separation domain size on the order of 1 to 3.7 nm in the materials. Both the electron density contrast between the two phases and the period lengths of the system increase as the content of UPy motifs in the hard phase increases, as shown in Fig. S6. This can demonstrate that the strong hydrogen bonding of UPy provides a stronger driving force for microphase separation³⁵. The microphase separated structure of DSE systems was further certified by atomic force microscopy (AFM), as shown in Fig. 2b. The AFM images showed the separation of soft phase (dark areas) and hard phase (bright areas) that are even-distributed and the increasing aggregation of the hard phase with the increasing UPy groups. On account of the microphase separation of the soft and hard domains in the nanometer dimension and the amorphous system, the DSE samples exhibit excellent transparency, as shown in Fig. 2c. The thickness of the DSE films was $\sim 500 \mu\text{m}$ and the transmittance is higher than 90% in the visible light region. The differential scanning calorimetry (DSC) traces for DSE-0 to DSE-3 was shown in Fig. 2d. It can be seen that the glass transition temperature (T_g) of all DSE samples keeps a very low constant around $-76 \text{ }^\circ\text{C}$ that is the T_g of PTMEG, suggesting that the lower T_g of DSE polymers derive from the local motions of the soft PTMEG domain and is independent of the UPy content in the DSE backbones. The result fits with “phase-locked” strategy, wherein “locking soft phase” PTMEG realizes Li-ion conduction in the DSE polymer systems. This would be discussed later. The thermal performance of DSE was further studied by thermal gravimetric analysis (TGA), which displayed that the four DSE samples was thermally stable up to $275 \text{ }^\circ\text{C}$ in Fig. S7.

Achieving both strength and self-healing through the synergistic interaction between HEDS and UPy

The mechanical properties of the resulting DSE materials were evaluated by tensile testing with an extension speed of 100 mm cm^{-1} at room temperature. Fig. 3a showed the tensile stress-strain curves of DSE samples, suggesting that all DSE materials exhibit **representative** elastic behavior because they do not display yielding phenomena during elongation. Based on a reasonable structure design, DSE materials possess impressive mechanical properties, such as superior tensile strength, stretchability and toughness, which vary greatly depending on the amount of UPy crosslinks embedded in the polymer backbones. An increase in UPy content contributes to a high improvement in tensile strength and toughness and a slight decrease in stretchability. Without UPy crosslinks, DSE-0 displayed highest stretchability of 2884.58% and weaker tensile strength of 9.62 MPa. When the UPy content increased to 30 mol %, DSE-3 exhibited optimal mechanical performance with a maximum stress up to 42.60 MPa and a high stretchability of 1630.53%. As calculated toughness in Fig. S8, DSE-3 possessed highest toughness of 259.9 MJ m^{-3} . The high stretchability and toughness may be derived from the increasing strong quadruple H-bonding UPy motifs as physical crosslinking in the polymer backbones. In the unstretched state, the interchain loops lead to the folding of the polymer backbones. When stretched, a

considerable chain extension occurs due to the extensive soft segments and the broken weak H-bonding interactions. The reversible nature of UPy moieties and dynamic S-S bonds under further stretching would bring about the opening of interchain rings and the unfolding and sliding of the polymeric backbones, thus improving the stretchability and toughness of DSE (Fig. 1a). Fig. 3b showed consecutive cyclic tensile behavior of DSE-3, which was stretched to 300% for five successive loading-unloading cycles. The first cycle exhibited a large hysteresis loop, then, the hysteresis loops of the subsequent cycles 2-5 slightly decreased with the increase of cycles and nearly overlapped with some signs of hysteresis, manifesting the continuous reorganization of dynamic supramolecular interactions. These observations demonstrate that the UPy cross-linking dissociation caused by mechanical strain is a mechanism of strain energy dissipation, a key feature of high toughness. DSE was observed to dissipate mechanical energy during stretching, as manifested by the large hysteresis in the cyclic stress-strain curves. Although different strain (100%, 300%, 500%) was applied on the toughest sample (DSE-3), it still exhibited a remarkable hysteresis and an apparent residual strain and the hysteresis increasing progressively with an increasing extension, which is due to the fact that the breakage of S-S bonds and multiple H-bonds cannot recover to their original state in the limited time (Fig. S9).

On account of the synergistic interaction between dynamic covalent disulfide metathesis (HEDS) and reversible supramolecular quadruple H-bonds (UPy)^{59,60} in the hard domain, DSE is expected to confer self-healing capability at room temperature. To visualize the excellent self-healing property of DSE materials, Fig. 3c showed that the scratch on the DSE-2 film was observed and finally faded away within 12 h at room temperature. Meanwhile, DSE-2 was chosen to evaluate the full-cut self-healing capability of DSE materials. The original dumbbell DSE-2 was fully cut into two pieces and then put them into contact at ambient condition for different times and at 60 °C for 2 h. Fig. 3d depicts the representative stress-strain curves for the original and recombined films at room temperature for different healing times and at higher temperature 60 °C for 2 h with the tensile rate of 100 mm min⁻¹. The self-healing DSE-2 can be able to reach a 3.07 MPa tensile strength and 604.76% tensile strain, along with 14.76% self-healing efficiency of toughness at room temperature for 2 h. Upon increasing healing time, the ultimate self-healing stress can reach almost 92.76% and the strain mostly overlapped with that of the original sample after 48 h. The self-healing process can be accelerated by raising temperature, while a healing temperature of 60 °C for 2 h brought about the recovery efficiency of 79.80% tensile strength and 89.40% stretching strain. The observed temperature-dependent self-healing performance is attributed to the easier occurrence of dynamic disulfide bonds exchange reaction and the easier recombination of multiple H-bonding interactions in multiphase polymer chains at higher temperature. The self-healing ability of the DSE systems mainly depends on dynamic disulfide bonds and multiple H-bonding interactions between polymer chains (Fig. 1b).

To gain a deeper insight into the bulk performance of DSE materials, time-temperature superposition (TTS) rheology experiments were carried out. Fig. 3e showed the shear modulus of the DSE materials from 10⁻¹⁰ to 10³ rad s⁻¹. It can be observed that the modulus for the rubber plateau is similar to all DSE. At the crossover frequencies (ω_c) between the storage (G') and loss (G'') modulus is the location where G'

$(\omega_c) = G''(\omega_c)$, that is, the relaxation time ($1/\tau_f$) of chain segments, the DSE polymers experience a transition from viscous state to rubber state. At low frequency, G'' is higher than G' , indicative of the viscosity behavior is predominant. As the frequency increases, G' increases faster than G'' , meaning that the elastomer property is ascendant at the $\omega > \omega_c$ region. The increasing amount of UPy in the DSE backbones from 0 to 30% results in a higher rubber plateau and longer chain relaxation time, which corresponds with the increasingly strong UPy H-bonding crosslinking density. Accordingly, the crossover points of G' and G'' of DSE move to higher frequency, indicating that DSE-3 is more “rubber-like” than DSE-0 at higher frequency. These results demonstrate that DSE materials mainly exhibit elastic behavior at room temperature, which is consistent with the lower T_g of DSE. As shown in Fig. S10, DMA curves presented temperature dependences of the storage modulus (G') and the loss factor ($\tan \delta$) for the DSE materials. The remarkable drops in G' relating to the relaxation of soft segments were all distinct and the four strong relaxation peaks appeared in the $\tan \delta$ curves, which could be assigned to T_g ⁵⁵. At temperature above T_g , a second continuous decrease in the storage modulus G' occurred for DSE samples. This phenomenon was also reported by Kim et al.⁶¹, manifesting that the hard phase domains have a tendency to rearrange at room temperature, which is beneficial to self-healing process.

Li-ion transport mechanism of DSICE

To study the “phase-locked” strategy, DSICE, denoted as DSICE-10 to DSICE-40, was created by dissolving different amount of LiTFSI from 10 wt.% to 40 wt.% into the DSE polymers and casting a film (Fig. S11). Ion transport properties were investigated through electrochemical impedance spectroscopy (EIS) and DSC traces. Fig. 4a showed the ionic conductivity of DSICE specimens. Experimentally, 35 wt.% LiTFSI was chosen to obtain the maximum value, up to $3.77 \times 10^{-3} \text{ S m}^{-1}$ at 30 °C, calculated by the equation $\sigma = L/SR$, where L corresponds to the thickness of DSICE samples, S corresponds to the effective overlap area, and R corresponds to the bulk resistance (Fig. S12). DSICE exhibited higher conductivity with the increasing temperature, as shown in Fig. S13, which can be attributed to more intense movements of polymer chains and ions at higher temperature. Li-ion transport behavior in the DSE polymers was demonstrated in Fig. 4b and Fig. S14, which presented that the ionic conductivity for DSICE with the same content 35 wt.% LiTFSI in the DSE-0~3 polymers remains relatively constant as the amount of quadruple UPy H-bonding increases. The similarity in the ionic conductivities of the DSE samples suggests that the Li-ion conduction is governed by the soft PTMEG segments and irrelevant to the hard UPy motifs. Further investigations confirmed the Li-ion transport mechanism. Fig. 4c depicts the T_g -dependent Li-ion transport behavior. The elevated T_g temperature along with the increasing amount of LiTFSI is due to the restricted movement of polymer chains caused by the coordination of Li^+ with the soft PTMEG segments. This strongly suggests that Li^+ dissociation environment in the DSICE materials derive from the soft PTMEG segments and the UPy groups do not interfere in the Li^+ dissociation and transport, that is, all the DSE macromolecules dissociate and transport Li^+ similarly^{52,62}. These observations and results demonstrate that the “locking soft phase” realizes Li-ion transport and provides ionic conductivity.

Mechanical properties and thermal stability of DSICE

The mechanical properties of DSICE is an important consideration for the application of the flexible ionic devices. Addition of LiTFSI salt causes a certain decrease in the mechanical properties of DSICE, which may be due to the large size of the TFSI anions interfering with chain packing and thus preventing aggregation of the UPy domains^{52,63}. Fig. 4d was the photographs of an DSICE-30 test specimen before and after stretching to 2000%. The stress-strain curves of DSICE, inside which was the local enlarged view, were showed in Fig. 4e. It can be observed that all DSICE exhibit exceptional strength and stretchability, of which stretching strength can reach up to 27.83 MPa and stretch strain can be more than 2000% of the original length. As the amount of LiTFSI increases, the mechanical strength decreases and the stretch strain increases. This is due to the loose polymer chains stacking caused by the increasing TFSI anions. Fig. 4f showed toughness of DSICE, of which DSICE-10 was maximum 164.36 MJ m⁻³ and DSICE-30 reached 79.20 MJ m⁻³. Combing with ionic conductivity, the preferable choice for the high-performance DSICE is DSICE-30 with 30 wt.% LiTFSI, which competes with the highest reported ionic conductors^{5,8,9,26-29,46,47}, as shown in Table S2. In addition, Fig. S15 exhibits excellent thermal stability of DSICE, of which possess high decomposition temperature, up to 230 °C. The operating temperature of DSICE-30 was assessed by rheological measurements upon a frequency sweep, as shown in Fig. S16. When the temperature is low, such as 30 °C, G' is much higher than G'', indicative of the perfectly elastic response of the materials. The crossover point of G' and G'' appears at the sweep temperature over 60 °C, suggesting that the **viscous** response starts to happen. Furthermore, the crossover point moves to the high-frequency direction as the sweeping temperature increases to 90 °C, meaning that the obvious **viscous** behavior occurs in the DSICE system. In order to make DSICE behavior more elastically, it is suggested that the operating temperature do not exceed 90 °C.

Autonomous self-healing capability and recyclable performance of DSICE

The self-healing capability in mechanical performance was investigated. To visualize the excellent self-healing abilities of the DSICE samples, the dumbbell-shaped DSICE-30 film colored blue and red with standard 12 mm × 2 mm rectangular and a thickness of 0.5 mm was cut into two pieces, respectively, then put any two colored pieces into contact and subsequently self-healed quickly at ambient temperature. After self-healing for 5 min, the jointed sample can be bent, twisted and even stretched to 100%, 400%, 800% of the original specimen, as shown in Fig. 5a and Movie S1. The optical microscope image of the self-healed sample was shown in Fig. S17, which displayed seamless combination of two cut-off pieces. The self-healing effect on mechanical performance was quantitatively evaluated by uniaxial tensile experiments. Dumbbell-shaped DSICE-30 specimens were bisected, and then recombined under different conditions. Fig. 5b presented the typical stress-strain curves of DSICE-30 specimens after from 30 min to 6 h healing time at ambient temperature. When the healing time was over 6 h, the stretch strength and strain of self-healed samples could recover to 10.13 MPa and 2172.64 %, respectively, which were almost coincident with original specimens, suggesting that DSICE were endowed with excellent autonomous self-healing capability. which ascribed the critical contribution of the reversible nature of dynamic S-S bonds and supramolecular H-bond motifs. From the point of view of molecular level, the

dynamic bonds existing on or near damaged area could promote the chains exchange reaction once contact occurs. Meanwhile, the low T_g of DSICE ($< -45\text{ }^\circ\text{C}$) makes them in a high elastic state and enhances the movement of polymer chains at room temperature, which could facilitate self-healing.

The reversible nature of dynamic S-S metathesis and supramolecular H-bonds in the polymer chains contributes to the recyclable performance of DSICE. Therefore, we further study the recyclable feature of DSICE through recycling in the THF solvent and reprocessing under compression molding conditions. Typically, Fig. 5c showed good recycling of DSICE, that is, DSICE can be fully dissolved into the THF solvent, recycled by casting the solution and drying, and then reprocessed into the desired specimens. Besides, the small pieces DSICE samples were hot-pressed in a mold applying a force of 0.5 MPa at $70\text{ }^\circ\text{C}$ for 30 min, reprocessing into an integrate and coherent film, as shown in Fig. 5d. Interestingly, transparent and smooth films of DSICE were obtained even after three times reprocessing or recycling. To further reveal the mechanical properties of reprocessed DSICE, tensile tests were performed. As shown in Fig. S18, the reprocessed DSICE-35 showed slightly decreased stretching stress, which is attributed to the insufficient crosslinking of the UPy units after the recycling process.

DSICE-based flexible conductive substrate and stretchable touch sensor

Transparent DSICE with highly competitive properties (see Fig 5e and Table S2) can be used to fabricate flexible iontronic devices, such as ionic conductive substrate and stretchable touch sensor. DSICE-based conductive substrate was visualized via “LED-lights” experiment, as shown in Fig. 6a. We placed a “heart-shaped” pattern with 18 LED lights on the DSICE-30 substrate. As expected, the “heart-shaped” pattern with LED lights can be entirely lit in an electric field. When DSICE-30 was cut from the middle of the “heart-shaped” pattern, the LED lights on either side of the “heart-shaped” pattern could not be lit. Then the cut-off DSICE-30 was contacted and self-healed for 30 min at room temperature, on which the “heart-shaped” pattern with 18 LED lights would be lit up again, and the luminescence intensity did not decay, which demonstrates DSICE-based conductive substrate with self-healing capacity could extend the service life of devices.

Fig. 6b was the schematic diagram of DSICE-based touch sensor in four different states: original, touched, stretched, stretched and touched. Human body can act as an ionic conductor. When a finger touches the sensor, the human body become part of the circuit, the finger can conduct current and introduce new elements into the circuit, causing the change of the circuit characteristics⁸. As shown in Fig. 6c, 6d, when the sensor was stretched, the $|Z|$ (impedance value) increased and the $-\phi$ (negative phase angle) changed slightly; when touched, the $|Z|$ and $-\phi$ versus frequency curves showed significant discrepancy from original or stretched states, i.e., the $|Z|$ exhibited a large peak in the frequency range of 100 Hz–1 MHz, the $-\phi$ changed a lot from positive value ($\sim 87^\circ$) to negative value ($\sim -20^\circ$) in the same frequency range. Obviously, the $-\phi$ became negative values at low frequency range (10 kHz to 100 Hz), so the touched sensor exhibited inductance characteristics. Fig. 6e presented the differences in the complex plane in the Nyquist plots of the impedance spectra under the four different states. In order to detect signals from different stimulus we set a single frequency ($f = 3\text{ kHz}$), as shown in Fig. 6E, different

stimulus appeared at different regions in impedance complex plane, meaning that the sensor responds very selectively to different stimulus. Fig. S19 depicted the impedance changes of DSICE-30 when stretched to different tensile elongation, as seen in Movie S2. And Fig. S20 depicted the impedance changes of DSICE-30 at different touched stimuli when stretched, as seen in Movie S3.

Discussion

In summary, based on the transport mechanism of lithium ion in polymer and the dynamic supramolecular engineering, we developed a novel ionic conductor, dynamic supramolecular ionic conductive elastomers, DSICE, by “locking soft phase” PTMEG conducting ions transport and regulating the dynamic metathesis HEDS and supramolecular quadruple UPy H-bonds in the hard phase achieving the excellent mechanical properties and self-healing capability. In addition, the rational molecular design endows DSICE high optical transparency and favorable recyclability. With these outstanding attributes, we demonstrated its application for a flexible conductive substrate and a stretchable touch sensor which was employed impedance spectra and impedance complex plane to analyze the different stimulus. Our elaborate designed DSICE opens up new frontiers in developing advanced ionic conductors with multiple functions and offers a promising material for the emerging flexible and wearable ionotronic devices or solid-state batteries.

Materials And Methods

Materials

Polytetramethylene ether glycol (PTMEG, $M_n = 2000$) was purchased from RHAWN. Hydrogenated 4,4'-methylenediphenyl diisocyanate (HMDI) was purchased from Aladdin. Bis(2-hydroxyethyl) disulfide (HEDS, tech. 90%) was purchased from Alfa Aesar. 2-ureido-4-pyrimidone (UPy) was prepared according to the published procedures⁶⁴. The catalyst dibutyltin dilaurate (DBTDL, tech. 95%) was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%) power was purchased from Aladdin and dried under vacuum at 100 °C for 24 h and subsequently put into an argon-filled glove box before use. The dry solvents N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were all obtained from a VSPS-5 solvent purification system. The anhydrous dimethyl sulfoxide (DMSO, 99.7%) was purchased from RHAWN.

Synthesis of DSE

The synthetic route of dynamic supramolecular elastomers (DSE) was shown in Fig. S1. PTMEG (2 g, 1 mmol) in a dried glass vessel was heated and stirring in an oil bath at 120 °C under vacuum (<133 Pa) for 1 h to remove any moisture, and then cooled to 65 °C. HMDI (0.55 g, 2.1 mmol) dissolved in dry DMF (10 mL) and one drop of DBTDL catalyst were dropwise added into the vessel and stirred for 1.5 h under N₂ atmosphere to yield prepolymer. After synthesis of the prepolymer, the final products were obtained via

adding different ratios of HEDS and UPy in the same polymerization procedure. HEDS (154.25 mg, 1 mmol) in appropriate amount of dry DMSO was added to the prepolymer solution. With fully stirring at 75 °C for another 9 h, methanol (1 mL) was added and the mixture was further stirred for 30 min to ensure the consumption enough of isocyanate groups. Then, the as-prepared solution was poured into a glass plate with subsequently putting in an oven at 60 °C to slowly evaporate the solvent overnight. Finally, the resulting film, named DSE-0, was dried in a vacuum oven at 60 °C for 24 h to obtain a transparent, colorless elastomer. Similarly, DSE-1, DSE-2, and DSE-3 were obtained by adding HEDS (138.82 mg, 0.9 mmol) and UPy (16.9 mg, 0.1 mmol), HEDS (123.40 mg, 0.8 mmol) and UPy (33.8 mg, 0.2 mmol) and HEDS (107.97 mg, 0.7 mmol) and UPy (50.7 mg, 0.3 mmol) in appropriate amount of dry DMSO.

Preparation of DSICE

DSE polymers were dissolved in appropriate amount of THF along with different amount of vacuum-dried LiTFSI. After fully dissolved, the viscous transparent solution was degassed and cast into a Teflon mold, and allowed to slowly evaporate at room temperature overnight. Then the resulting film was further dried for 24 h at 60 °C in a vacuum oven. The obtained films were 50-500 μm thickness and named as DSICE.

Materials characterization

ATR-FTIR was performed on a Nicolet 6700 IR spectrometer (Thermo Scientific, USA) equipped with a diamond ATR crystal mode from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and scanning time of 32. **$^1\text{H NMR}$** (400 MHz) spectra were recorded on a Bruker AVANCE δ spectrometer at room temperature using the deuterated CDCl_3 solvent as the lock field. **Raman** spectra (Renishaw) of the obtained DSE samples were recorded on a microscope using a laser excitation wavelength of 532 nm. The spectra were collected over a spectral range from 2000 to 100 cm^{-1} . The integration time was 20 s, and the accumulation number was 2. **GPC** tests were conducted using a Shimadzu LC-20AD GPC system with the 35 °C. THF was used as the mobile phase with flow rate of 1 mL min^{-1} . **DSC** experiments were carried out under N_2 atmosphere using a TA Instrument DISCOVER DSC 250 system. All the samples (~5 mg) were heated from -120 to 50 °C at a scan rate of 10 °C min^{-1} . **Small-angle x-ray scattering (SAXS)** measurements on polymer films were performed on a SAXS point 2.0 instrument (Anton Paar, Austria) equipped with a Cu/Mo dual microfocal X-ray source and a two-dimensional hybrid photon counting detector (EIGER R 1M). Transmittance of the films were carried out using **UV-vis** spectrophotometer (PE Lambda950, China) with the wavelengths for testing ranging from 800 to 400 nm. All the samples were 0.5 mm thickness. The microphase structure of the samples on microsubstrate were measured by tapping-mode **atomic force microscopy (AFM, Bruker, INNOVA)** using tapping MPP-rotated cantilevers with silicon probes. The thermal stability property was evaluated by **thermogravimetric analysis (TGA)** with a differential thermal analysis instrument (METTLER TOLEDO TGA/DSC3+) over the

temperature range of 25 ~ 600 °C in N₂ atmosphere with a heating rate of 10 °C min⁻¹ (empty Al₂O₃ crucible as the reference). The **rheological** behavior was carried out on a MCR302 (Anton Paar, Graz, Austria) rheometer. Frequency and temperature sweeps were performed with 25 mm parallel plate attachment. All the samples, approximately 0.5-0.8 mm thickness, were conducted dynamic amplitude sweep experiments to confirm their linear region. Master curves were built using time-temperature superposition (TTS). Frequency sweeps were performed at 0.1 Hz – 100 Hz, and temperature sweeps were run from 30 °C to 170 °C, with the strain automatically modulated at 5% ± 2% by the instrument to make sure the measured torque at a reasonable value as the sample softened. The reference temperature is 30 °C. **Dynamic mechanical analysis (DMA)** of DSE samples were performed on a Netzsch DMA242E system with a tension mode. The rectangular samples were cut into 10 mm × 4 mm × 0.4 mm (length × width × thickness) and heated from -130 to 50 °C at a 3 °C min⁻¹ heating rate and a constant frequency of 1 Hz.

Mechanical Properties Tests

The mechanical performance was mainly evaluated via stress-strain curves. The stress-strain experiments were performed using a TianYuan (TY-8000) Electronic Universal Test Instrument with a 50 N force transducer. The whole samples were cut into a dumb-bell shape (a testing size of 12.0 × 2.0 × 0.5 mm³) for tensile tests. All the testing rate was set at 100 mm min⁻¹.

Ion Conductivity Investigation

Ion conductivity of DSICE was calculated by the following formula: $\sigma = L/SR$, where L (cm) is the thickness of DSICE membrane ($\approx 240 \mu\text{m}$ and measured by the thickness gauge), R (Ω) is the bulk resistance of DSICE membrane obtained from electrochemical impedance spectroscopy (EIS), and S (cm²) is the contact area of the electrode and DSICE membrane. The DSICE membranes were sandwiched between two stainless steel (SS) electrodes with a diameter of 16 mm. EIS was measured using a ParStat4000 electrochemical workstation (Princeton, America) over the temperature range from 30 °C to 70 °C, and the frequency range was set from 0.1 Hz to 1 MHz with amplitude of 10 mV.

Self-healing Capability Measurements

The visual self-healing results were observed by optical microscopy (OM). The complete fracture self-healing ability was evaluated by stress-strain curves. The dumbbell samples were completely cut in half, then the two pieces of all samples were manually contacted. After self-healing at different conditions, the healed samples were subjected to tensile tests.

Impedance Tests

The impedance tests were performed on a broadband dielectric/impedance spectrometer (Novocontrol GmbH). The samples were 1mm thickness, the testing copper electrodes were diameter of 30 mm, testing V_{rms} (voltage effective value) was set at 1 V. The samples were treated without metal spraying on

surfaces. For testing touch sensors, the impedance tests were performed on an electrochemical workstation (CHI660E), testing V_{rms} was set at 0.5 V.

Fabricating of touch sensors

The DSICE was cut to a shape of $50.0 \times 50.0 \times 1.0 \text{ mm}^3$. Two aluminum electrodes were then attached at both ends of the DSICE for testing. For the touched measuring, finger touched on the middle of the sensor without pressing. The sensor was stretched to twice of the original length for the stretched measuring.

References

1. C. Larson, B. Peele, S. Li, S. Robinson, M. Totaro, L. Beccai, B. Mazzolai, R. Shepherd, Highly stretchable electroluminescent skin for optical signaling and tactile sensing. *Science* **351**, 1071–1074 (2016).
2. S. Lin, H. Yuk, T. Zhang, G. A. Parada, H. Koo, C. Yu, X. Zhao, Stretchable hydrogel electronics and devices. *Adv. Mater.* **28**, 4497–4505 (2016).
3. C. Yang, Z. Suo, Hydrogel ionotronics. *Nat. Rev. Mater.* **3**, 125–142 (2018).
4. J. H. Kim, K. G. Cho, D. H. Cho, K. Hong, K. H. Lee, Ultra-sensitive and stretchable ionic skins for high-precision motion monitoring. *Adv. Funct. Mater.* **31**, 2010199 (2021).
5. H. D. Xuan, B. Timothy, H.-Y. Park, T. N. Lam, D. Kim, Y. Go, J. Kim, Y. Lee, S. I. Ahn, S.-H. Jin, J. Yoon, Super stretchable and durable electroluminescent devices based on double-network ionogels. *Adv. Mater.* **33**, 2008849 (2021).
6. T. Li, X. Zhang, S. D. Lacey, R. Mi, X. Zhao, F. Jiang, J. Song, Z. Liu, G. Chen, J. Dai, Y. Yao, S. Das, R. Yang, R. M. Briber, H. L. Cellulose ionic conductors with high differential thermal voltage for low-grade heat harvesting. *Nat. Mater.* **18**, 608–613 (2019).
7. C.-C. Kim, H.-H. Lee, K. H. Oh, J.-Y. Sun, Highly stretchable, transparent ionic touch panel. *Science* **353**, 682–687 (2016).
8. L. Shi, T. Zhu, G. Gao, X. Zhang, W. Wei, W. Liu, S. Ding, Highly stretchable and transparent ionic conducting elastomers. *Nat. Commun.* **9**, 2630 (2018).
9. J. Lee, M. W. M. Tan, K. Parida, G. Thangavel, S. A. Park, T. Park, P. S. Lee, Water-processable, stretchable, self-healable, thermally stable, and transparent ionic conductors for actuators and sensors. *Adv. Mater.* **32**, 1906679 (2020).
10. Z. Cao, H. Liu, L. Jiang, Transparent, mechanically robust, and ultrastable ionogels enabled by hydrogen bonding between elastomers and ionic liquids. *Mater. Horiz.* **7**, 912–918 (2020).
11. H. J. Kim, B. Chen, Z. Suo, R. C. Hayward, Ionoelastomer junctions between polymer networks of fixed anions and cations. *Science* **367**, 773–776 (2020).
12. X. Pu, M. Liu, X. Chen, J. Sun, C. Du, Y. Zhang, Z. J., W. Hu, Z. Wang, Ultrastretchable, transparent triboelectric nanogenerator as electronic skin for biomechanical energy harvesting and tactile sensing. *Sci. Adv.* **3**, e1700015 (2017).

13. K. Parida, V. Kumar, W. Jiangxin, V. Bhavanasi, R. Bendi, P. S. Lee, Highly transparent, stretchable, and self-healing ionic-skin triboelectric nanogenerators for energy harvesting and touch applications. *Adv. Mater.* **29**, 1702181 (2017).
14. Y. Ren, J. Guo, Z. Liu, Z. Sun, F. Yan, Ionic liquid-based click-ionogels. *Sci. Adv.* **5**, eaax0648 (2019).
15. Y. Ding, J. Zhang, L. Chang, X. Zhang, H. Liu, L. Jiang, Preparation of high-performance ionogels with excellent transparency, good mechanical strength, and high conductivity. *Adv. Mater.* **29**, 1704253 (2017).
16. K. G. Cho, S. An, D. H. Cho, J. H. Kim, J. Nam, M. Kim, K. H. Lee, Block copolymer-based supramolecular ionogels for accurate on-skin motion monitoring. *Adv. Funct. Mater.* **31**, 2102386 (2021).
17. X. Liu, C. Steiger, S. Lin, G. A. Parada, J. Liu, H. F. Chan, H. Yuk, N. V. Phan, J. Collins, S. Tamang, G. Traverso, X. Zhao, Ingestible hydrogel device. *Nat. Commun.* **10**, 493 (2019).
18. M. Vázquez-González, I. Willner, Stimuli-responsive biomolecule-based hydrogels and their applications. *Angew. Chem., Int. Ed.* **59**, 15342–15377 (2019).
19. B. Yiming, X. Guo, N. Ali, N. Zhang, X. Zhang, Z. Han, Y. Lu, Z. Wu, X. Fan, Z. Jia, S. Qu, Ambiently and mechanically stable ionogels for soft ionotronics. *Adv. Funct. Mater.* **31**, 2102773 (2021).
20. Z. Yu, P. Wu, A highly transparent ionogel with strength enhancement ability for robust bonding in an aquatic environment. *Mater. Horiz.* **8**, 2057–2064 (2021).
21. J.-Y. Sun, X. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak, Z. Suo, Highly Stretchable and Tough Hydrogels. *Nature* **489**, 133–136 (2012).
22. K. J. Henderson, T. C. Zhou, K. J. Otim, K. R. Shull, Ionically cross-linked triblock copolymer hydrogels with high strength. *Macromolecules* **43**, 6193–6201 (2010).
23. R. H. Stokes, R. A. Robinson, Ionic hydration and activity in electrolyte solutions. *J. Am. Chem. Soc.* **70**, 1870 (1948).
24. Y. Yanagisawa, Y. Nan, K. Okuro, T. Aida, Mechanically robust, readily repairable polymers via tailored noncovalent cross-linking. *Science* **359**, 72–76 (2018).
25. P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* **451**, 977–980 (2013).
26. M. Wang, Z. Lai, X. Jin, T. Sun, H. Qi, Multifunctional liquid-free ionic conductive elastomer fabricated by liquid metal induced polymerization. *Adv. Funct. Mater.* **31**, 2101957 (2021).
27. R. Li, T. Fan, G. Chen, K. Zhang, B. Su, J. Tian, M. He, Autonomous self-Healing, antifreezing, and transparent conductive elastomers. *Chem. Mater.* **32**, 874–881 (2020).
28. C. Dang, F. Peng, H. Liu, X. Feng, Y. Liu, S. Hu, H. Qi, Facile solvent-free synthesis of multifunctional and recyclable ionic conductive elastomers from small biomass molecules for green wearable electronics. *J. Mater. Chem. A* **9**, 13115–13124 (2021).
29. B. Yiming, Y. Han, Z. Han, X. Zhang, Y. Li, W. Lian, M. Zhang, J. Yin, T. Sun, Z. Wu, T. Li, J. Fu, Z. Jia, S. Qu, A mechanically robust and versatile liquid-free ionic conductive elastomer. *Adv. Mater.* **33**,

- e2006111 (2021).
30. M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, Optically healable supramolecular polymers. *Nature* **472**, 334–337 (2011).
 31. D. W. R. Balkenende, C. A. Monnier, G. L. Fiore, C. Weder, Optically responsive supramolecular polymer glasses. *Nat. Commun.* **7**, 10995 (2016).
 32. K. Liu, L. Cheng, N. Zhang, H. Pan, X. Fan, G. Li, Z. Zhang, D. Zhao, J. Zhao, X. Yang, Y. Wang, R. Bai, Y. Liu, Z. Liu, S. Wang, X. Gong, Z. Bao, G. Gu, W. Yu, X. Yan, Biomimetic impact protective supramolecular polymeric materials enabled by quadruple H-bonding. *J. Am. Chem. Soc.* **143**, 1162–1170 (2021).
 33. M. Rottger, T. Domenech, R. V. D. Weegen, A. Breuillac, R. Nicolay, L. Leibler, High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **356**, 62–65 (2017).
 34. W.-X. Liu, Z. Yang, Z. Qiao, L. Zhang, N. Zhao, S. Luo, J. Xu, Dynamic multiphase semi-crystalline polymers based on thermally reversible pyrazole-urea bonds. *Nat. Commun.* **10**, 4753 (2019).
 35. Y. Lai, X. Kuang, P. Zhu, M. Huang, X. Dong, D. Wang, Colorless, transparent, robust, and fast scratch-self-healing elastomers via a phase-locked dynamic bonds design. *Adv. Mater.* **30**, 1802556 (2018).
 36. J. Hentschel, A. M. Kushner, J. Ziller, Z. Guan, Self-healing supramolecular block copolymers. *Angew. Chem., Int. Ed.* **124**, 10713–10717 (2012).
 37. H. Ying, Y. Zhang, J. Cheng, Dynamic urea bond for the design of reversible and self-healing polymers. *Nat. Commun.* **5**, 3218 (2014).
 38. M. A. Ratner, D. F. Shriver, Ion transport in solvent-free polymers. *Chem. Rev.* **88**, 109–124 (1988).
 39. M. Li, C. Wang, Z. Chen, K. Xu, J. Lu, New concepts in electrolytes. *Chem. Rev.* **120**, 6783–6819 (2020).
 40. Z. Guan, J. T. Roland, J. Z. Bai, S. X. Ma, T. M. McIntire, M. Nguyen, Modular domain structure: A biomimetic strategy for advanced polymeric materials. *J. Am. Chem. Soc.* **126**, 2058–2065 (2004).
 41. R. O. Ritchie, The conflicts between strength and toughness. *Nat. Mater.* **10**, 817 (2011).
 42. E. Ducrot, Y. Chen, M. Bulters, R. P. Sijbesma, C. Creton, Toughening elastomers with sacrificial bonds and watching them break. *Science* **344**, 186–189 (2014).
 43. J.-C. Lai, L. Li, D.-P. Wang, M.-H. Zhang, S.-R. Mo, X. Wang, K.-Y. Zeng, C.-H. Li, Q. Jiang, X.-Z. You, J.-L. Zuo, A rigid and healable polymer cross-linked by weak but abundant Zn(II)-carboxylate interactions. *Nat. Commun.* **9**, 2725 (2018).
 44. X. Liao, M. Dulle, E. S. De Souza, J. M., R. B. Wehrspohn, S. Agarwal, S. Forster, H. Hou, P. Smith, A. Greiner, High strength in combination with high toughness in robust and sustainable polymeric materials. *Science* **366**, 1376–1379 (2019).
 45. Z. Lei, P. Wu, A highly transparent and ultra-stretchable conductor with stable conductivity during large deformation. *Nat. Commun.* **10**, 3429 (2019).

46. X. Qu, W. Niu, R. Wang, Z. Li, Y. Guo, X. Liu, J. Sun, Solid-state and liquid-free elastomeric ionic conductors with autonomous self-Healing ability. *Mater. Horiz.* **7**, 2994–3004 (2020).
47. W. Zhang, B. Wu, S. Sun, P. Wu, Skin-like mechanoresponsive self-healing ionic elastomer from supramolecular zwitterionic network. *Nat. Commun.* **12**, 4082 (2021).
48. Y. Gu, S. Zhang, L. Martinetti, K. H. Lee, L. D. McIntosh, C. D. Frisbie, T. P. Lodge, High toughness, high conductivity ion gels by sequential triblock copolymer self-assembly and chemical cross-linking. *J. Am. Chem. Soc.* **135**, 9652–9655 (2013).
49. S. Zhang, K. H. Lee, C. D. Frisbie, T. P. Lodge, Ionic conductivity, capacitance, and viscoelastic properties of block copolymer-based ion gels. *Macromolecules* **44**, 940–949 (2011).
50. S. A. Chopade, J. G. Au, Z. Li, P. W. Schmidt, M. A. Hillmyer, T. P. Lodge, Robust polymer electrolyte membranes with high ambient-temperature lithium-ion conductivity via polymerization-induced microphase separation. *ACS Appl. Mater. Interfaces* **9**, 14561–14565 (2017).
51. M. W. Schulze, L. D. McIntosh, M. A. Hillmyer, T. P. Lodge, High-modulus, high-conductivity nanostructured polymer electrolyte membranes via polymerization-induced phase separation. *Nano Lett.* **14**, 122–126 (2014).
52. Y. Chen, A. M. Kushner, G. A. Williams, Z. Guan, Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* **4**, 467–472 (2012).
53. D. G. Mackanic, X. Yan, Q. Zhang, N. Matsuhisa, Z. Yu, Y. J. Jiang, T. Manika, J. Lopez, H. Yan, K. Liu, X. Chen, Y. Cui, Z. Bao, Decoupling of mechanical properties and ionic conductivity in supramolecular lithium ion conductors. *Nat. Commun.* **10**, 5384 (2019).
54. Q. Zhang, S. Niu, L. Wang, J. Lopez, S. Chen, Y. Cai, R. Du, Y. Liu, J.-C. Lai, L. Liu, C.-H. Li, X. Yan, C. Liu, J. B.-H. Tok, X. Jia, Z. Bao, An elastic autonomous self-healing capacitive sensor based on a dynamic dual crosslinked chemical system. *Adv. Mater.* **30**, 1801435 (2018).
55. D. Wang, J. Xu, J. Chen, P. Hu, Y. Wang, W. Jiang, J. Fu, Transparent, mechanically strong, extremely tough, self-recoverable, healable supramolecular elastomers facilely fabricated via dynamic hard domains design for multifunctional applications. *Adv. Funct. Mater.* **30**, 1907109 (2020).
56. J. Kang, D. Son, G.-j. N. Wang, Y. Liu, J. Lopez, Y. Kim, J. Y. Oh, T. Katsumata, J. Mun, Y. Lee, L. Jin, J. B.-H. Tok, Z. Bao, Tough and water-insensitive self-healing elastomer for robust electronic skin. *Adv. Mater.* **30**, 1706846 (2018).
57. D. G. Mackanic, W. Michaels, M. Lee, D. Feng, J. Lopez, J. Qin, C. Yi, Z. Bao, Crosslinked poly(tetrahydrofuran) as a loosely coordinating polymer electrolyte. *Adv. Energy Mater.* **8**, 1800703 (2018).
58. L. Dong, X. Zeng, J. Fu, L. Chen, J. Zhou, S. Dai, L. Shi, Cross-linked ionic copolymer solid electrolytes with loose coordination-assisted lithium transport for lithium batteries. *Chem. Eng. J.* **423**, 130209 (2021).
59. R. P. Slijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, Reversible polymers formed from self-complementary monomers using quadruple hydrogen bonding. *Science* **29**, 1601–1604 (1998).

60. S. H. M. Sontjens, R. P. Sijbesma, M. H. P. Van Genderen, E. W. Meijer, Stability and lifetime of quadruply hydrogen bonded 2-ureido-4[1H]-pyrimidinone dimers. *J. Am. Chem. Soc.* **122**, 7487–7493 (2000).
61. S. Kim, H. Jeon, S. Shin, S. Park, J. Jegal, S. Y. Hwang, D. X. Oh, J. Park, Superior toughness and fast self-healing at room temperature engineered by transparent elastomers. *Adv. Mater.* **30**, 1705145 (2017).
62. B. Qiao, G. M. Leverick, W. Zhao, A. H. Flood, J. A. Johnson, Y. Shao-Horn, Supramolecular regulation of anions enhances conductivity and transference number of lithium in liquid electrolytes. *J. Am. Chem. Soc.* **140**, 10932–10936 (2018).
63. Y. Tominaga, K. Yamazaki, V. Nanthana, Effect of anions on lithium ion conduction in poly(ethylene carbonate)-based polymer electrolytes. *J. Electrochem. Soc.* **162**, A3133-A3136 (2015).
64. S. H. Söntjens, R. A. E. Renken, G. M. L. V. Gemert, T. A. P. Engels, A. W. Bosman, H. M. Janssen, L. E. Govaert, F. P. T. Baaijens, Thermoplastic elastomers based on strong and well-defined hydrogen-bonding interactions. *Macromolecules* **41**, 5703–5708 (2008).

Declarations

Acknowledgments

Funding: This research was supported in part by the National Natural Science Foundation of China (No. 51973171), and Young Talent Support Plan of Xi'an Jiaotong University. Natural Science Basic Research Program of Shaanxi (No. 2020JC-09), China Postdoctoral Science Foundation (2019M663687), Fundamental Research Funds for the Central Universities (xhj032021014-02, and xjh012020042).

Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Figures

Figure 1

Schematic illustration of the molecular design and mechanism of dynamic supramolecular ionic conductive elastomers (DSICE) with superior stretchability and toughness, autonomous self-healing. (a) The molecular structure design and the proposed mechanism for the superior tough DSICE upon stretching. (b) The synergistic interaction of multiple dynamic bonds contributes to autonomous self-healing capability.

Figure 2

Microphase structures of transparent dynamic supramolecular elastomers with varying amounts of UPy motifs (DSE-0~3). (a) SAXS profile plots of DSE-0~3 that demonstrates the presence of microphase separation on the order of 1 to 3.7 nm. (b) AFM phase images of DSE-0~3. The dark areas represent the soft phase and the bright areas represent the hard phase, indicative of the microphase separation structure of DSE-0~3. (c) Transmittance of DSE-0~3 in the visible range. Insert: Photograph of the as-synthesized DSE, suggesting the high transparency of DSE. (d) DSC traces of DSE-0~3. The constant T_g at around $-76\text{ }^\circ\text{C}$ is displayed

Figure 3

Mechanical properties and self-healing capability of DSE. (a) Typical stress-strain curves of DSE 0~3. Deformation rate: 100 mm min^{-1} . Maximum strain and stress reach 1630.53% and 42.60 MPa for DSE-3 with a 30% UPy motif, respectively. (b) Consecutive cyclic tensile behavior of DSE-3 at a strain of 300%. The apparent hysteresis is responsible for the great energy dissipation capacity of DSE, a key feature for high toughness. (c) Optical microscopy images of the scratched and healed DSE-2 film. Healed condition: 12 h at ambient environment. (d) Stress-strain curves of the original and self-healed DSE-2 specimens after different healing time from 2 h to 48 h at r. t. and $60\text{ }^\circ\text{C}$ for 2 h. Deformation rate: 100 mm min^{-1} . (e) Time-temperature superposition (TTS) rheology of DSE-0~3.

Figure 4

Li-ion transport mechanism and mechanical properties of DSICE. (a) Ionic conductivity of DSICE varying the amount of LiTFSI from 10 wt.% to 40 wt.% at $30\text{ }^\circ\text{C}$. The ionic conductivity of DSICE-35 reaches the maximum value of $3.77 \times 10^{-3}\text{ S m}^{-1}$. (b) Ionic conductivity of DSE-0~3 with the same amount of 35 wt.% LiTFSI at $30\text{ }^\circ\text{C}$. The ionic conductivity of DSE-0~3 with 35 wt.% LiTFSI keeps almost consistent, suggesting that the ionic conductivity of DSICE originate from the soft phase and independent on the hard phase of the polymer backbone, thereby demonstrating “phase-locked” strategy of DSICE. (c) DSC traces of DSICE-10~40. T_g of DSICE elevates along with the increasing amount of LiTFSI, indicating that the introduction of LiTFSI leads to the restricted movement of polymer chains caused by the coordination of Li^+ with the soft PTMEG segments. (d) Digital graph of stretchability of DSICE-30. DSICE can be stretched to $>2000\%$ of the original sample. (e) Typical stress-strain curves of DSICE-10~40. Deformation rate: 100 mm min^{-1} . Insert: local enlarged view of low strain region of the stress-strain curve. (f) Toughness of DSICE-10~40.

Figure 5

Autonomous self-healing capability and multiple recyclability of DSICE. (a) Tensile curves of the original and self-healed DSICE-30 sample after different healing time from 30 min to 6 h at room temperature. (b) Photograph of DSICE-30 before and after self-healing. The colored dumbbell DSICE-30 was cut into two pieces and then put any two pieces into contact. After self-healed for 10 min, the jointed sample can be bent, twisted and even stretched to 100%, 400%, 800% of the original specimen. (c) Recycling of DSICE. In the direction of arrow: irregular DSICE; irregular DSICE was dissolved in THF and stirred for 2 h to form homogenous solution; Reformation of DSICE after the solvent completely removed. (d) Recycled DSICE sample via hot-pressing (Condition: 70 °C, 0.5 MPa, 30 min). (e) Comparison of the overall performance between this work and recently reported typical ionic conductor materials.

Figure 6

DSICE-based flexible conducting substrate and stretchable touch sensor. (a) Visually demonstration of DSICE as conducting substrate with excellent self-healing capacity to extend the service life. From left to right: A “heart-shaped” pattern with 18 LEDs was placed on the DSICE-30 substrate; LEDs were lit in an electric field; DSICE-30 sample was cut from the middle of the “heart-shaped” pattern and LEDs were out; after self-healed for 30 min, LEDs were lit again. (b) Schematic diagram of DSICE-based touch sensor at different states (original, touched, stretched, stretched and touched). (c) Plots of impedance magnitude ($|Z|$) versus testing frequency of touch sensor at different states. (d) negative phase angle ($-\phi$) versus testing frequency of touch sensor at different states. (e) Nyquist plots of impedance spectra of touch sensor at different states. (f) Repeatedly detected data of touch sensor at a single frequency ($f = 3$ kHz) in impedance complex plane (original, gray dots; touched, red dots; stretched, blue dots; stretched and touched, green dots).

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supplementarymaterials.docx](#)
- [movieS1.mp4](#)
- [movieS2.mp4](#)
- [movieS3.mp4](#)