

Supplementary Materials for

Mechanochromic and Ionic Conductive Cholesteric Liquid Crystal Elastomers for Biomechanical Monitoring and Human-Machine Interaction

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1. Experimental Procedures

1.1 Materials

The diacrylate LC monomer RM257 and chiral dopant LC756 were purchased from Jiangsu Hecheng Display Technology Co., Ltd. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), 2,2'-(Ethylenedioxy)diethanethiol (EDDET), 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA), Dipropylamine (DPA), Irgacure 651, [2-(Acryloyloxy)ethyl]trimethylammonium chloride (ATAC) solution (80 wt% in water), 2,2-Diethoxyacetophenone (DEAP), Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), Poly(ethylene glycol) diacrylate (PEGDA, $M_n \sim 308 \text{ g mol}^{-1}$) were purchased from Sigma-Aldrich. Butyltrimethylammonium chloride ($[N_{4111}] \text{ Cl}$) was purchased from Meryer. Toluene was obtained from J&K Scientific Ltd. All chemicals were used as received.

1.2 Preparation of Ionic Liquid

The ionic liquid was prepared following procedures reported in the literature.^[1] Firstly, 2.18 g ATAC solution and 2.93 g Li [TFSI] were mixed in 10 mL deionized water, and the reaction was vigorously stirred for 2 h. Subsequently, the resulting oil was washed 5 times with deionized water to remove LiCl and other residues, and then was vacuum dried at 70 °C for 12 h to obtain a transparent [ATAC][TFSI]. The preparation procedure of $[N_{4111}][\text{TFSI}]$ is the same as that of [ATAC][TFSI], except that ATAC was replaced by $[N_{4111}] \text{ Cl}$.

1.3 Preparation of Polymer Ionic Liquid Network

The polymer ionic liquid networks were prepared as follows: 438.4 mg [ATAC][TFSI] (1 mmol), 297.3 mg $[N_{4111}][\text{TFSI}]$ (0.75 mmol), PEGDA (1.0 μL), TMSPMA (0.2 μL) and photoinitiator DEAP (2.0 μL) were thoroughly mixed. Then, the precursor was poured into the Teflon mold. After polymerization with UV light (365 nm, 20 W cm^{-2}) for 10 min under N_2 environment, the polymer ionic liquid networks were obtained.

1.4 Silane Coupling to Polymer Ionic Liquid Network

The surface of the polymer ionic liquid networks was modified by grafting a functional silane coupling agent. The as-prepared PILNs were coated with 200 μL of TMSPMA solution (2 wt % in a 1:1 water-ethanol mixture) and incubated for 12 h at room temperature. Subsequently, the

PILNs were washed with ethanol, completely dried, and stored under low-humidity conditions. Due to the introduction of TMSPMA into the PILN precursor, a linkage was created between the silane group in the TMSPMA solution and that on the PILN surface, allowing the methacrylate groups of TMSPMA free to react with other monomers. Notably, because of the infiltration of trace water, the silane coupling agents in the PILNs were also hydrolyzed and condensed, which increased the crosslinking degree of the PILNs.

1.5 Preparation of iCLCE

The preparation of iCLCEs was based on the anisotropic deswelling method reported previously.^[2] Firstly, 630 mg RM257 and 29 mg LC756 were dissolved in 400 mg toluene and heated to 80 °C for 5 min. After cooling to 25 °C, 155 mg EDDET, 36.7 mg PETMP, and 4 mg I-651 were added into the solution. Finally, 180 mg DPA diluted in toluene at the ratio of 1:50 was added as a catalyst for the Michael addition reaction (first stage) and mixed well. The resulting solution was poured onto the PILN surface placed in the Teflon mold and left at 25 °C for 29 h. After the solvent evaporated completely, the iCLCE was irradiated with 365 nm UV light with an intensity of 50 mW cm⁻² for 5 min (second stage).

1.6 Characterization and Measurement

FTIR spectra were acquired using Thermo Scientific Nicolet iS20. POM images were taken with an Olympus BX60 in transmission mode for microscopic observation. The microstructures of iCLCEs were observed by Hitachi S4800 cold field emission scanning electron microscopy (SEM). 2D-WAXD experiment was conducted on Rigaku HomeLab. The reflection spectra were collected using an Ocean Optics Flame-T spectrometer. Mechanical experiments were performed by a universal mechanical tester (UTM2203, Shenzhen SUNS Technology Stock Co., Ltd.). The stress-strain tests were done with samples (40 mm × 5 mm × 0.6 mm) at a strain rate of 10 mm min⁻¹. The compression experiments were done with samples (10 mm × 10 mm × 0.6 mm) at a strain rate of 0.1 mm min⁻¹. The interfacial toughness of iCLCEs and various PILN-solid bonding was measured using the 90-degree peeling test apparatus. Samples of iCLCEs were prepared with the size of 80 × 20 × 1.2 mm. A 20 × 20 mm paraffin film was inserted at the CLCE–PILN interface and PILN–solid interface at one end, which prevents the bonding in the corresponding area and acts as a pre-crack. All 90-degree peeling tests were carried out at a constant peeling speed of 50

mm min⁻¹. The interfacial toughness was given by dividing the plateau force by the width of iCLCEs. The ionic conductivity was carried out using an electrochemical workstation (CHI660E) and was calculated according to the equation: $\sigma = L/(R \times S)$, where R, S, L are the bulk resistance, area, and thickness of PILN samples, respectively. The resistance and capacitance changes were measured by an LCR meter (TH2830) at 50 kHz sweep frequency and 1 V AC voltage.

2. Results and Discussion

2.1 Supplementary Figures

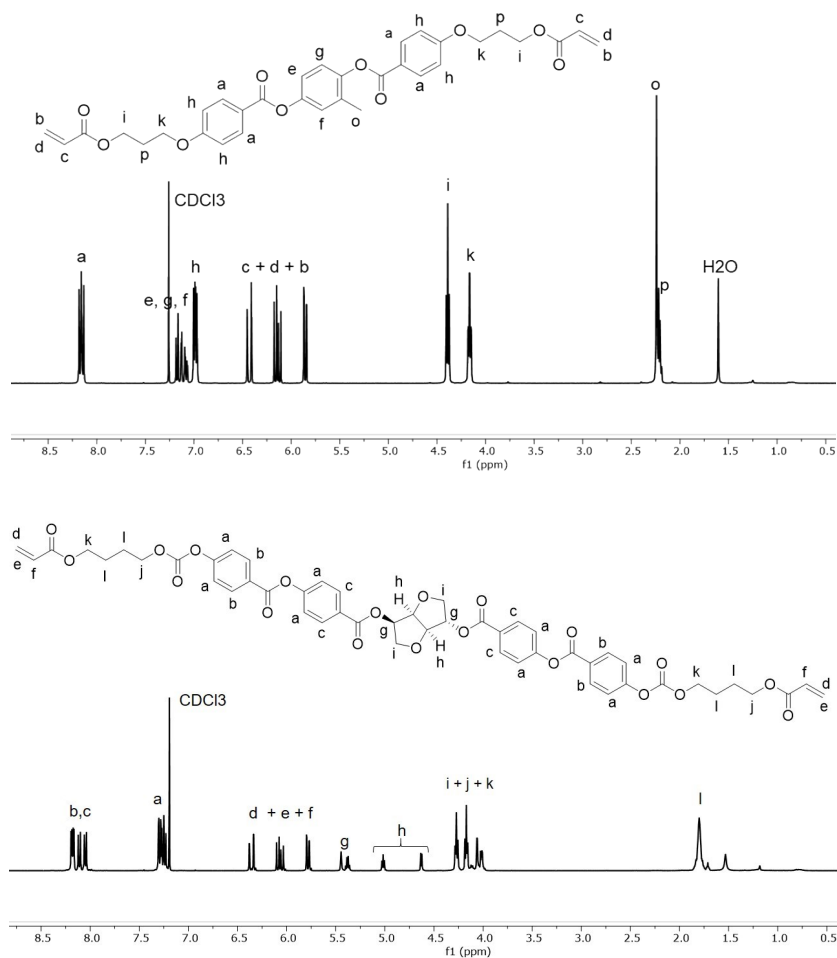


Fig. S1 ¹H NMR spectra of RM257 and LC756.

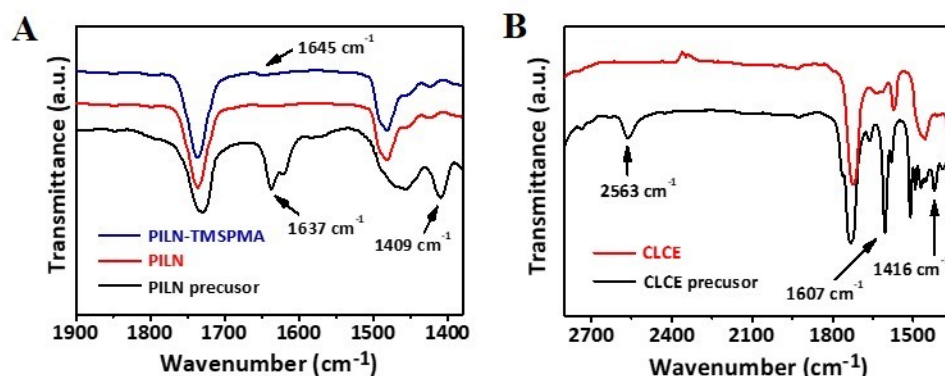


Fig. S2 FTIR spectra of each step of the iCLCE preparation. (A) FTIR spectra of the PILN layer. A disappearance of acrylate related bands at 1637 and 1409 cm⁻¹ is observed after polymerization, indicating that the polymerization process of the PILN is fully completed. Then the band at 1645 cm⁻¹ appears after surface treatment through grafting TMSPMA. (B) FTIR spectra of the CLCE layer. The disappearance of thiols related bands at 2563 cm⁻¹ and the disappearance of acrylate related bands at 1607 and 1416 cm⁻¹ are observed after two-stage thiol-acrylate Michael addition and photopolymerization reactions.

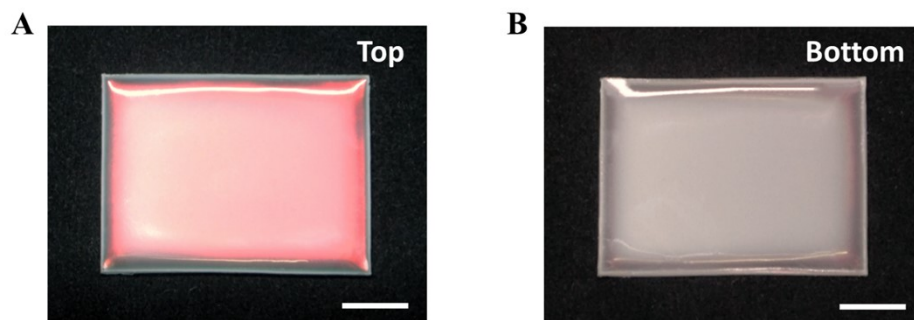


Fig. S3 Photographs of the iCLCE prepared by the anisotropic deswelling method. The upper layer (A) is the red-reflecting CLCE ($\approx 200 \mu\text{m}$ thickness). The red reflection is strongly seen from the top, but from the bottom, the film appears a dull grey-white due to strong scattering from a poorly aligned structure. The bottom layer (B) is the transparent polymer ionic liquid network ($\approx 400 \mu\text{m}$ thickness) (Scale bar = 1cm).

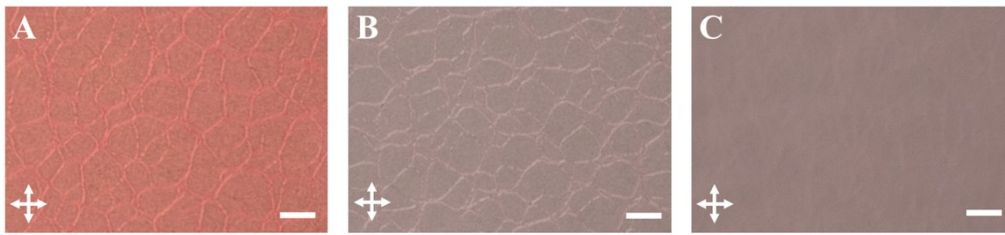


Fig. S4 POM images of the front (A) and back (at different focal lengths) (B and C) of the iCLCE (Scale bar = 100 μm).

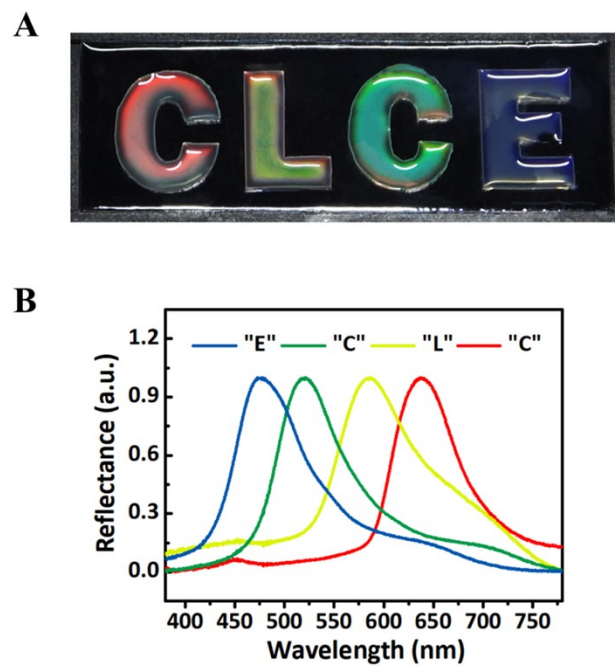


Fig. S5 iCLCEs with different patterns (A) and the corresponding reflection spectra (B).

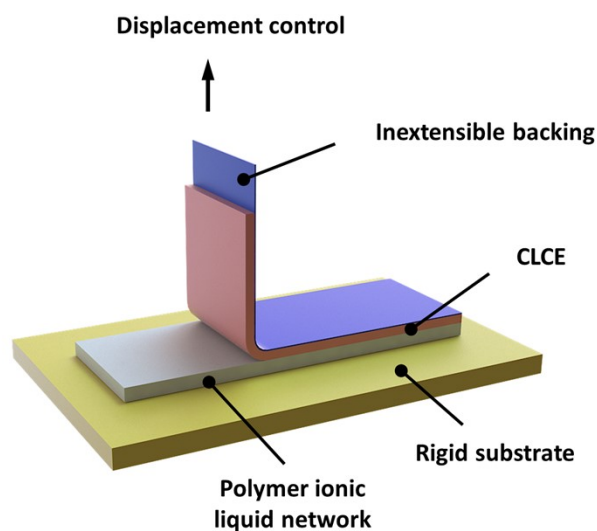


Fig. S6 Schematic illustration of the 90-degree peeling testing setup to test the interfacial toughness between the CLCE and the polymer ionic liquid network.

Table S1 Optimization of the interfacial toughness by varying the content of TMSPMA. Sample 3 was selected as the optimal recipe.

Samples	[ATAC][TFSI]: [N ₄₁₁₁][TFSI] (molar ratio)	PEGDA	[ATAC][TFSI]	[N ₄₁₁₁][TFSI]	DEAP	TMSPMA
1	1 : 0.75	1.0 μ L	1.0 mmol	0.75 mmol	2.0 μ L	0 μ L (0 % v/w)
2	1 : 0.75	1.0 μ L	1.0 mmol	0.75 mmol	2.0 μ L	0.04 μ L (0.01 % v/w)
3	1 : 0.75	1.0 μ L	1.0 mmol	0.75 mmol	2.0 μ L	0.2 μ L (0.05 % v/w)
4	1 : 0.75	1.0 μ L	1.0 mmol	0.75 mmol	2.0 μ L	0.4 μ L (0.1 % v/w)
5	1 : 0.75	1.0 μ L	1.0 mmol	0.75 mmol	2.0 μ L	2.0 μ L (0.5 % v/w)
6	1 : 0.75	1.0 μ L	1.0 mmol	0.75 mmol	2.0 μ L	4.0 μ L (1.0 % v/w)

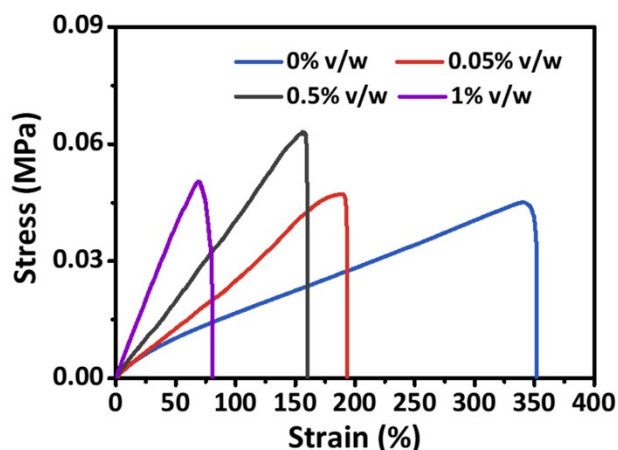


Fig. S7 Stress-strain curves of polymer ionic liquid networks with different contents of TMSPMA.

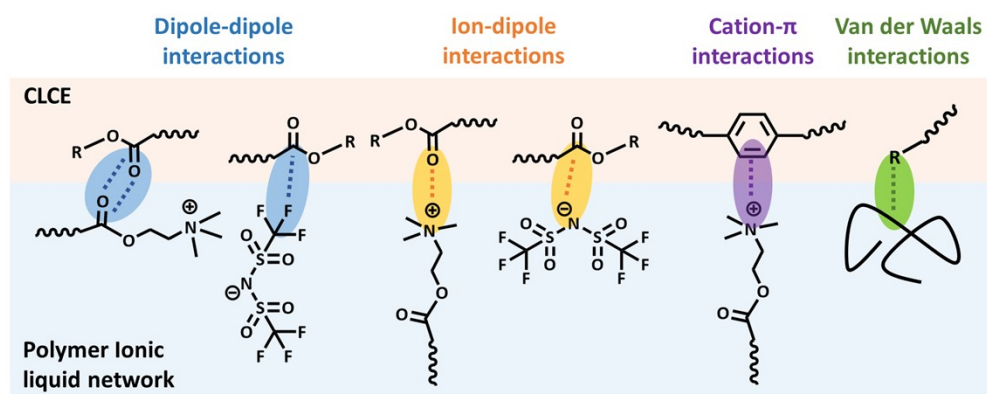


Fig. S8 The possible adhesion mechanisms between the CLCE and the polymer ionic liquid network.

Table S2 Optimization of the ionic liquid precursor composition by varying the molar ratio of [ATAC][TFSI] and [N₄₁₁₁][TFSI]. Sample 4 was selected as the optimal recipe.

Samples	[ATAC][TFSI]: [N ₄₁₁₁][TFSI] (molar ratio)	PEGDA	[ATAC][TFSI]	[N ₄₁₁₁][TFSI]	DEAP	TMSPMA (0.05 v/w %)
1	1 : 0.1	1.0 μL	1.0 mmol	0.1 mmol	2.0 μL	0.2 μL
2	1 : 0.25	1.0 μL	1.0 mmol	0.25 mmol	2.0 μL	0.2 μL
3	1 : 0.5	1.0 μL	1.0 mmol	0.5 mmol	2.0 μL	0.2 μL
4	1 : 0.75	1.0 μL	1.0 mmol	0.75 mmol	2.0 μL	0.2 μL

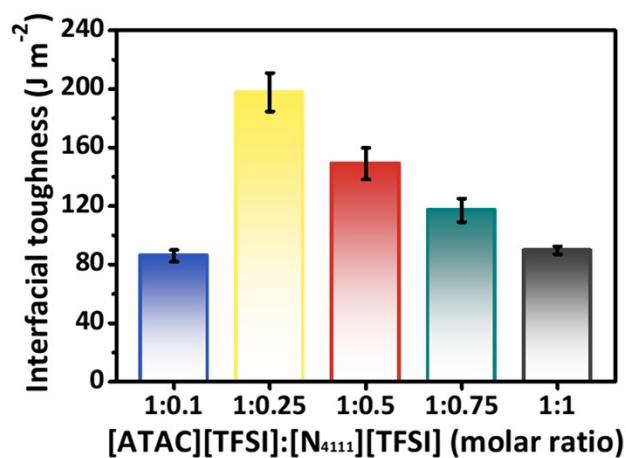


Fig. S9 Interfacial toughness of iCLCEs with different molar ratios of [ATAC][TFSI] and [N₄₁₁₁][TFSI].

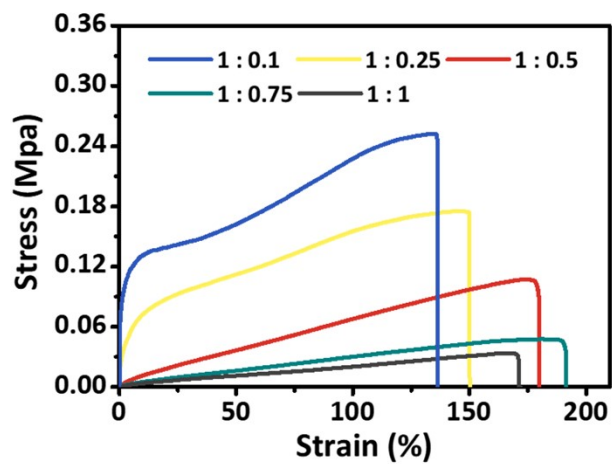


Fig. S10 Stress-strain curves of polymer ionic liquid networks with different molar ratios of [ATAC][TFSI] and [N₄₁₁₁][TFSI].

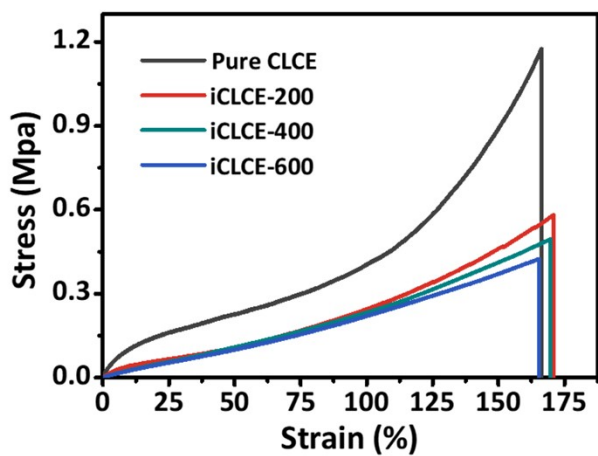


Fig. S11 Stress-strain curves of the pure CLCE (200 μm) and the iCLCEs with different thicknesses of PILNs (200, 400, and 600 μm).

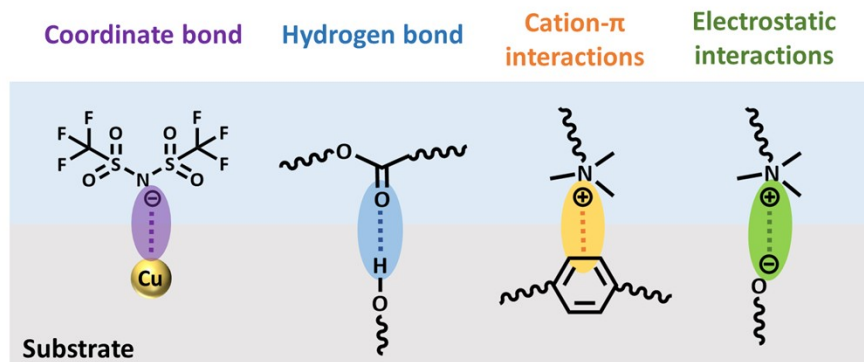


Fig. S12 Schematic adhesion mechanisms between the polymer ionic liquid network and substrates.

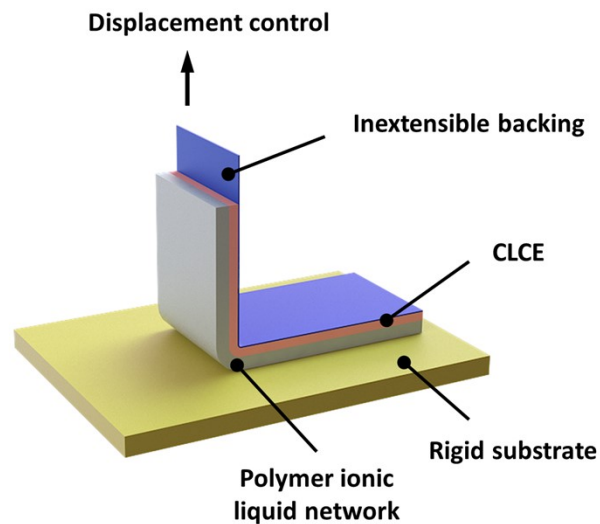


Fig. S13 Schematic illustration of the experimental setup of the 90-degree peeling test to test the interfacial toughness between the polymer ionic liquid network and substrates.

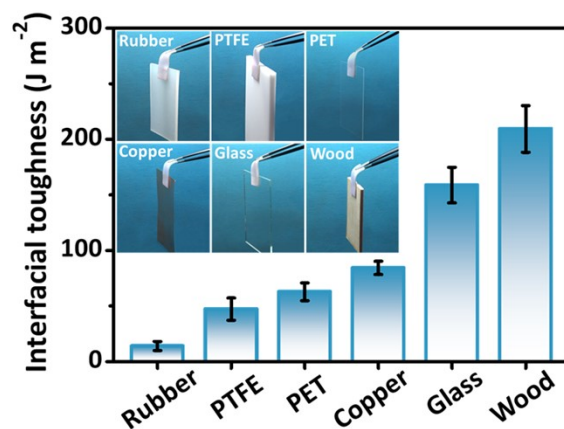


Fig. S14 Interfacial toughness of the iCLCEs with different substrates.

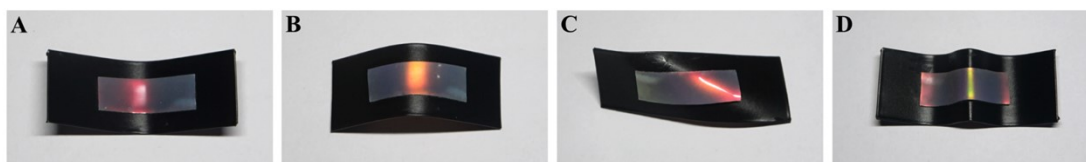


Fig. S15 Images of the iCLCE bonded to substrates with different arbitrarily distorted curvatures.

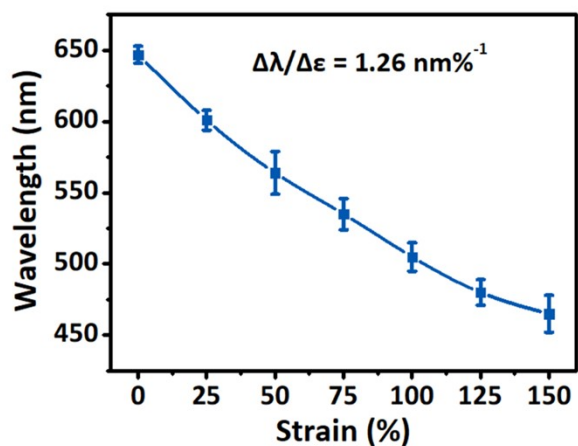


Fig. S16 Optical sensing sensitivity of the iCLCE upon mechanical stretching.

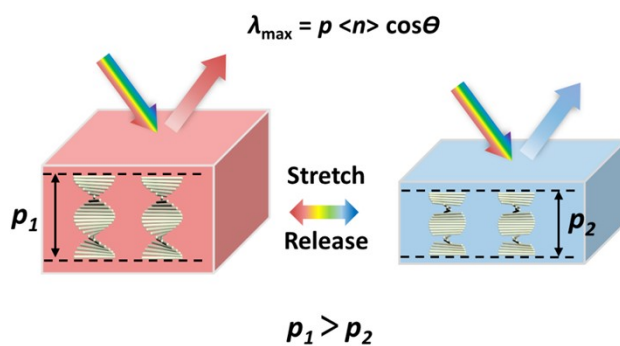


Fig. S17 The mechanochromic mechanism of iCLCEs during uniaxial stretching.^[3]

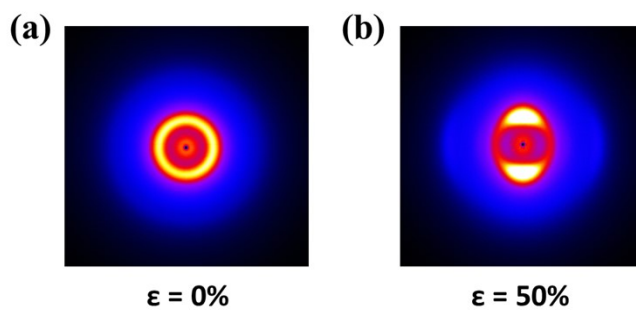


Fig. S18 2D-WAXD patterns of the CLCEs (a) at the initial state and (b) at a stretched state.

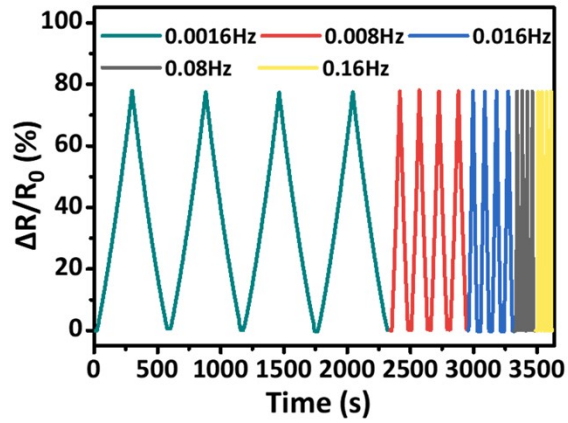


Fig. S19 Relative resistance changes with different stretching frequencies at 50% strain.

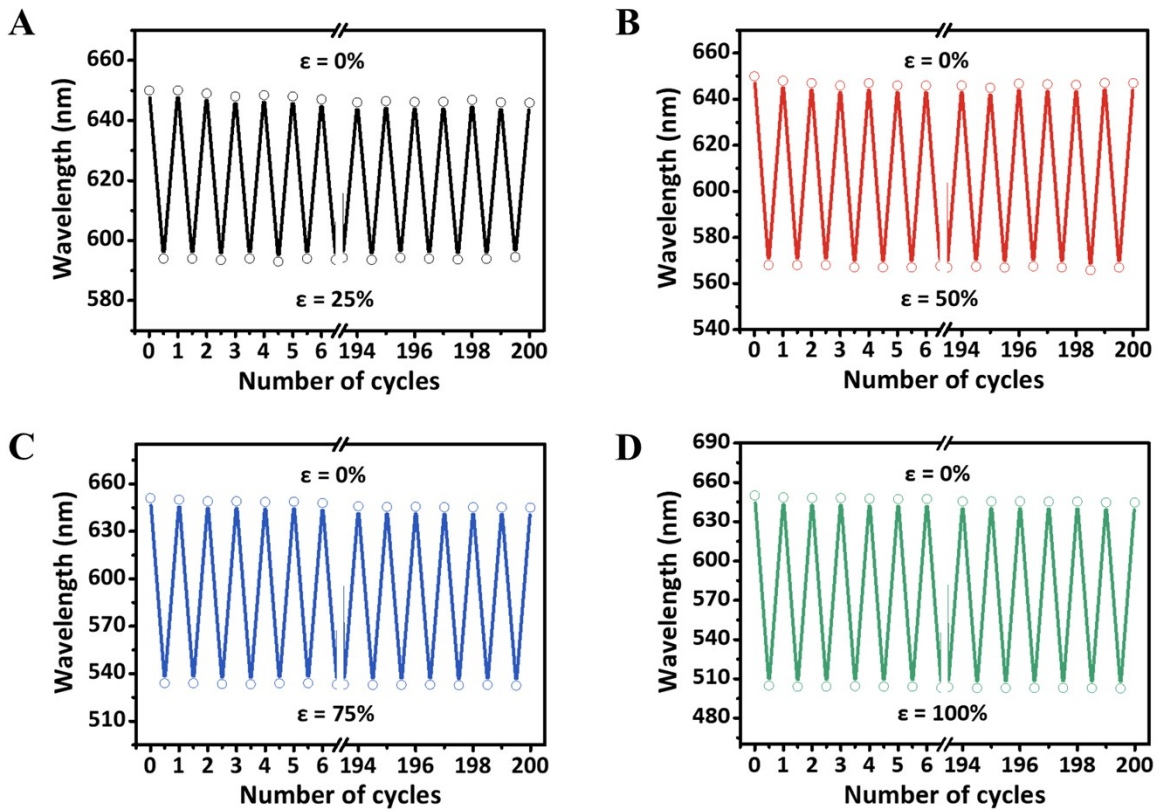


Fig. S20 Mechanochromic repeatability of the iCLCE under strains of 25% (A), 50% (B), 75% (C), and 100% (D).

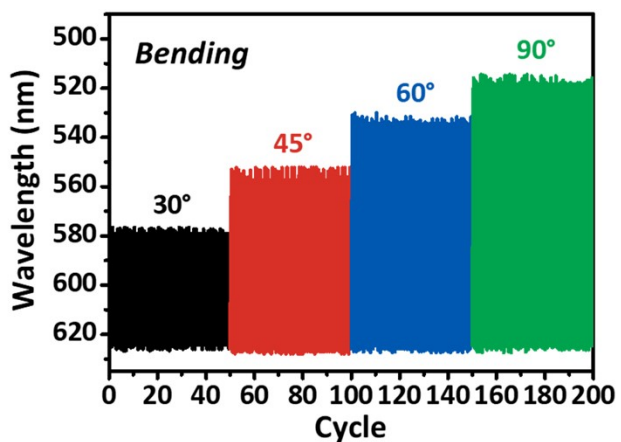


Fig. S21 Reflection-peak wavelengths of the iCLCE under cyclic changes of different angles of the finger.

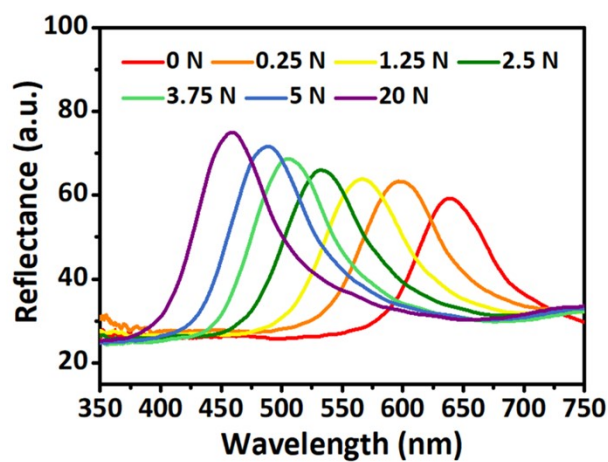


Fig. S22 Reflection spectra of the red-reflecting iCLCE at pressures from 0 to 20 N.

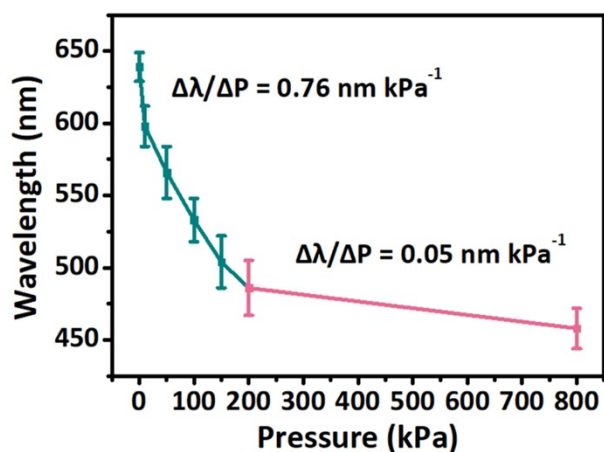


Fig. S23 Optical sensing sensitivity of the iCLCE under compression.

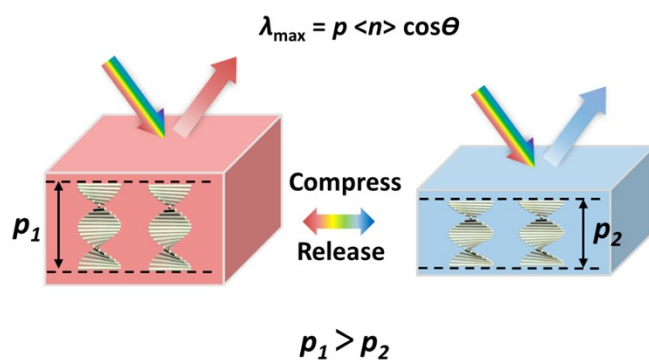


Fig. S24 The mechanochromic mechanism of compressed iCLCEs. Upon compressing, the color change toward shorter wavelength is induced by pitch contraction effect, which maintains the intrinsic helical structure of iCLCEs.^[4]

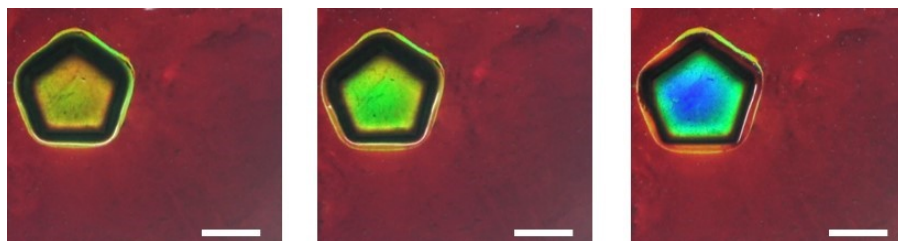


Fig. S25 The pictures of the capacitive sensor based on iCLCEs for displaying colour information to identify the shape and location of the pressure source (Scale bar = 5 mm).

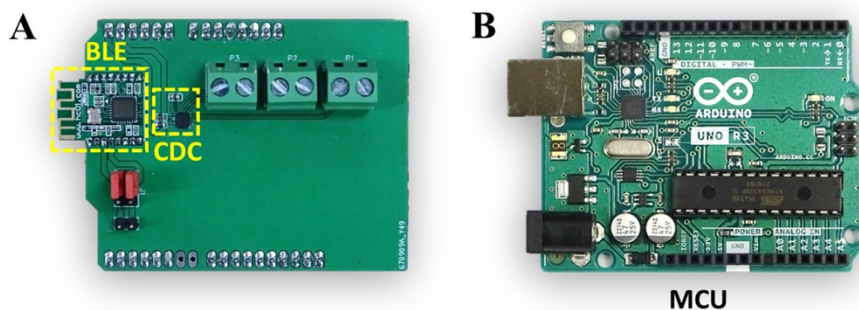


Fig. S26 Photographs of the measurement module. (A) CDC, capacitance-to-digital converter. BLE, bluetooth low energy. (B) MCU, microcontroller unit.

2.2 Supplementary Movies

Movie S1: Circularly polarized reflection and resistance changes of the iCLCE upon mechanical stretching.

Movie S2: Dynamic control of a virtual film in real time using the iCLCEs.

Movie S3: Motion control of a car in a video game using the RGB iCLCE array.

3. References

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