Electronic Supplementary Information

Poly(ionic liquid) Hydrogel-based Anti-freezing Ionic Skin for Soft Robotic Gripper

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**Synthesis of 1-vinyl-3-(methoxycarbonyl)-imidazole:**

Vinyl-3-(methoxycarbonyl)-imidazole was synthesized by stirring a mixture containing vinyl imidazole (14.10 g, 0.15 mol) and methyl chloroacetate (17.90 g, 0.165 mol) at room temperature for 2 days. The product was washed by diethyl ether 3 times and then dried under vacuum at 30 °C for 6 h, obtaining a white powder. $^1$HNMR (400 MHz, D2O) $\delta$ 7.7(d, 1H, CH$_2$=CH-N), 7.2 (s, 1H, CH$_2$=CH-N), 5.9 (s, 1H, N-CH=CH), 5.5 (s, 1H, N-CH=CH), 5.2 (d, 1H, N-CH$_2$-C), 3.8 (t, 1H, C-O-CH$_3$).

**Synthesis of 1-Vinyl-3-carboxylate-imidazol:**

1-Vinyl-3-carboxylate-imidazol was synthesized by adding 1-vinyl-3-(methoxycarbonyl)-imidazole (3.50 g, 0.017 mol) and KOH (1.07 g, 0.02 mol) into a solvent of ethanol (20 mL), stirring for 2 h. The product was separated by the centrifuge at a speed of 8000 r min$^{-1}$ for 5 min. Then dried the transparent solution will get the crude product. Finally, washed the crude product with ethanol 3 times and dried it at room temperature, obtaining the white powder. $^1$HNMR (400 MHz, D2O) (ppm): 7.7 (d, 1H, CH$_2$=CH-N), 7.2 (s, 1H, CH$_2$=CH-N), 5.8 (s, 1H, N-CH=CH), 5.4 (s, 1H, N-CH=CH), 4.8 (d, 1H, N-CH$_2$-C).
**Figure S1.** Comparative FT-IR spectra of AAm (red), IL monomer (1-vinyl-3-(carboxymethyl)-imidazolium) (green), and PIL (poly(1-vinyl-3-(carboxymethyl)-imidazolium)) gel (blue).

**Figure S2.** Transmittance spectra of the PIL gel in the visible range.
Figure S3. Differential scanning calorimetry (DSC) test of PAAm, PAAm/KCl and PIL gel. The tests were executed under nitrogen (20 ml min\(^{-1}\)) with a scan rate of 1 °C min\(^{-1}\).

Figure S4. a) Mean square displacement (MSD)-time curves of water near PAAm and PIL chains; b) survival time correlation functions of water near PAAm and PIL chains.
Figure S5. Design and characterization of the multimodal PIL-Skin. a) schematic diagram of the PIL-Skin structure and photograph of a normal PIL-Skin; b) tensile test of the PIL-Skin at room temperature (the strain rate is 30 mm min⁻¹ throughout the experiments); c) fabrication process of the PIL-Skin; d) self-healing process of the PIL-Skin; e) soft robotic gripper attached with a PIL-Skin.
Figure S6 a) Weight retention of the PIL gel and PIL-Skin at 60 °C; b) weight retention of the PIL gel and PIL-Skin at room environment (at 20 °C, RH of 20%).

Figure S7. Schematic diagram of the Triboelectric Nanogenerator (TENG). When an active object contacts a dielectric material (such as VHB), an electrification process occurs at the contact interface between the PIL-Skin and the oscillating PET ram. When the ram surface moves away from the PIL-Skin, a negative static charge in the dielectric
material induces migration of ions in the hydrogel to achieve electrostatic charge balance, leading to an electron transfer from the metal electrode to the ground. Similarly, when the ram moves back to contact with the PIL-Skin, this electron transfer and ion migration are reversed. Because the effective contacting area of the PIL-Skin and PTFE ram was different under varied pressures, high pressure can generate more electrostatic charges at the interface, resulting in the corresponding higher voltages and currents.