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Electronic Supplementary Information

Thermoresponsive ionogels with switchable adhesion in air and aqueous environments induced by LCST phase behavior

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Experimental Section

Materials

Butyl acrylate (BA) was purchased from Macklin. Ethyleneglycol dimethacrylate (EGDMA, crosslinker), diethoxyacetophenone (DEOP, photo-initiator) was purchased from Aladdin Industrial Corporation. Ionic liquids [1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf_2], >99%) and 1- propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([PrMIM][NTf_2], >99%)] were purchased from Lanzhou Yulu Fine Chemical Co., Ltd. All photo images in the current work were taken by the photo camera (Canon 60D).

Sample preparation

Butyl acrylate (monomer, a sequency of concentration of 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt% were prepared), EGDMA, (0.1 mol%, 0.2 mol%, 0.5 mol%, 0.8 mol%, 1.0 mol% of monomer amount)), and diethoxyacetophenone (DEOP) (0.1 wt% to monomers) were dissolved in ILs, and then the mixture was stirred for 10 min until a fully transparent solution was obtained. The polymerization was initiated by UV irradiation, and the solution was cured under UV light (365 nm, 800 mW/cm^2) for 15 min.

LCST characterization of ionogels

The LCST of ionogels was determined by optical transmittance measurements using dynamic light scattering (Litesizer™ 500; Anton Paar, Graz, Austria). A transmittance of 100% indicates ionogel homogeneity, and a decrease in transmittance suggests that the ionogels undergoes LCST phase separation. We define the LCST as the temperatures at which the transmittance drops to 80%.

Method for mechanical measurements

The mechanical characterization of ionogels was realized using a tensile machine (SUNS, UMT4103, Shenzhen, China). The sample were cut into dumbbell shape, 30 mm in length, 5 mm in width, 2 mm in height. Both ends of the dumbbell-shaped sample were connected to the clamps with the lower clamp fixed. The upper clamp was pulled by the load cell at a constant velocity of 20 mm/min at room temperature, by which the stress–strain curve was recorded and the experimental data were further analyzed. The tensile strength was obtained from the failure point.

Method for switchable adhesion tests in air and aqueous environments

Pull-off tests and lap shear tests were performed on a tensile machine system (SUNS, UMT4103, Shenzhen, China) at different temperature(25°C，45°C). In the lap shear test, a second substrate was overlapped with the first (at a lap shear joint of 1.0 cm × 0.5 cm) with no external pressure, and instant adhesion was tested. The adhesion was measured on the universal testing machine with a 100 N loading cell. Adhesion strength was obtained from the maximum force at joint failure divided by the overlap area. In the pull-off test, ionogel discs (2 mm in thick, 15 mm in diameter) were attached to substrates with controlled preloads in the range of 11–55 kPa. After the application of the preload, the motorized part was moved along the vertical axis with a pulling rate of 10 mm/min until the occurrence of separation at the ionogel/substrate interface. Adhesion strength was obtained from the maximum force at the occurrence of separation divided by the overlap area. For cycling adhesion tests, two methods were performed in a temperature-controlled chamber and the adhesion strength was measured in the cooled and heated state for five circles.

For the underwater switchable adhesion measurements, the substrates were affixed to the

bottom of a small water bath placed on the adhesion test equipment. The temperature was changed by controlling the water temperature. The ionogel disc was submerged in the water bath. After the application of the preload 11 kPa, the adhesion strength was measured by the pull-off tests. For cycling adhesion test, the underwater adhesion strength sequentially for 5 cycles was measured by the pull-off test at 25°C and then at 45°C.

The adhesion strength of ionogels in salt solution (1M NaCl) and acid solution (1M HCl) was measured by pull-off test. In this experiment, the experimental setup is used as the same as during underwater testing.

Water contact angle measurement

The water contact angles were measured using a Dataphysics (Germany) OCA20 contact-angle system at 25°C and 45°C，respectively. A 2 μL water droplet was carefully deposited on ionogel surfaces using a syringe.

Method for observing the extrusion and reabsorption of micro droplets on the ionogel surface

Ionogels were placed on a Peltier device to precisely control the temperature and were observed by a microscope and take a photo of the sample surface at different temperatures.

Method for friction measurement

The friction of an ionogel against PTFE substrates at 25°C and 60°C was measured using a rheometer (MCR302, Anton Paar) that operated in a compressive strain-controlled shear mode, respectively. The square-shaped ionogel, (2×2 cm^2, 3 mm in thickness) was affixed on the lower platen of the rheometer, and a discs-shaped PTFE substrate (15 mm in diameter, 2 mm in thickness) was affixed to the upper platen. Measurements were performed after the normal force F = 0.06N was applied, whereupon the shear stress σ was recorded and the coefficient of friction were is calculated as follows：

$$COF = \frac{F}{\sigma}$$

Supporting Figures

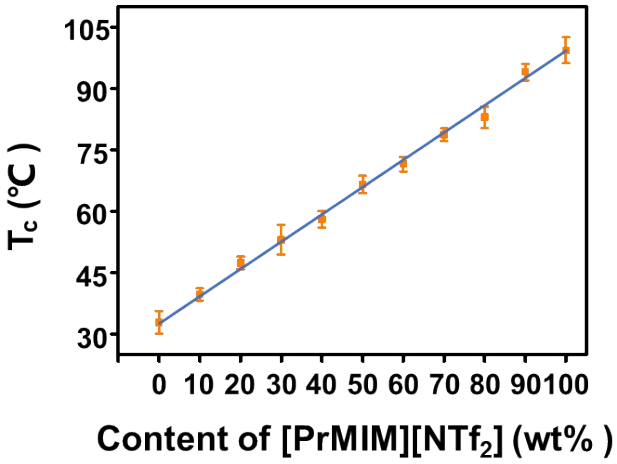

Figure S1. Phase separation temperatures (T_c) of ionogels as a function of [PrMIM][NTf_2] to [EMIM][NTf_2] proportion in the ionogels containing 60 wt% PBA.

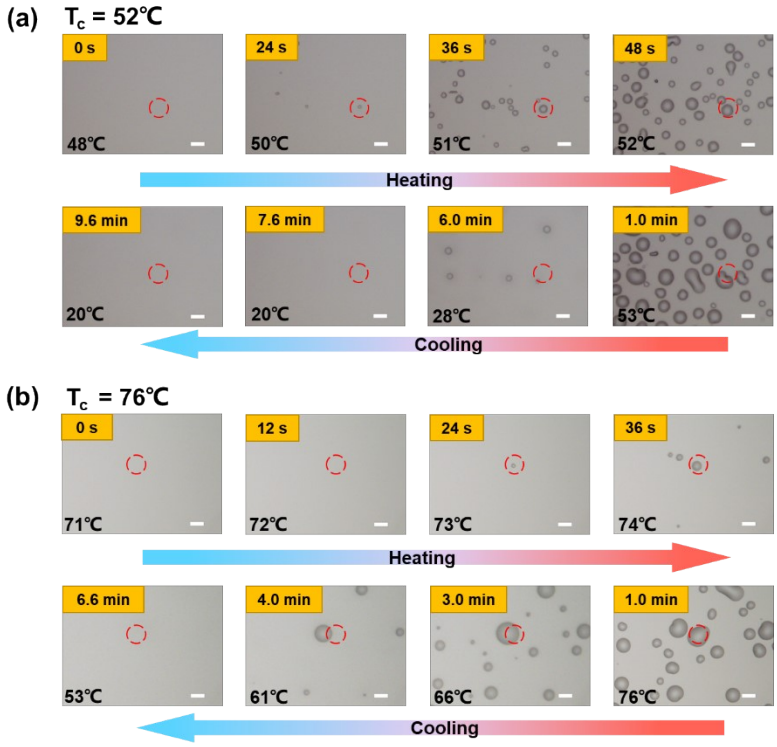

Figure S2. Optical microscope images respectively showing the extrusion and reabsorption of micro droplets on ionogel surfaces with T_c ~ 52°C (a) and T_c ~ 76°C (b) induced by LCST-type phase separation. Scale bar, 20 μm.

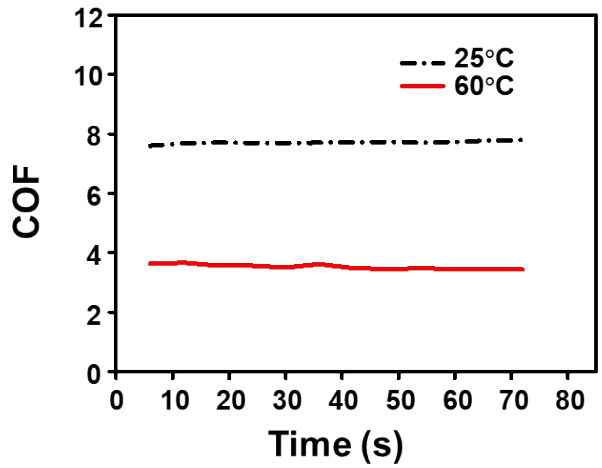

Figure S3. The coefficients of friction (COFs) of the ionogels (T_c ~ 32°C) at 25°C and 60°C on PTFE substrates with the normal force 0.06 N.

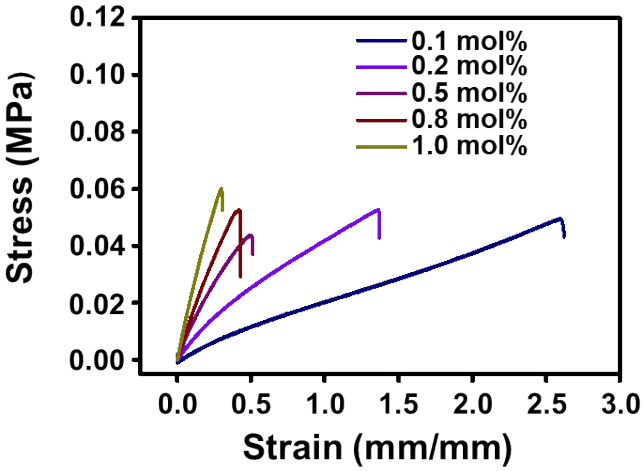

Figure S4. Tensile stress–strain curves of the ionogels with different crosslinking density.

The slope of the curves represents the modulus of the ionogels. As the crosslink density increases, the slope of curves becomes steeper, indicating the higher strength of the ionogels.

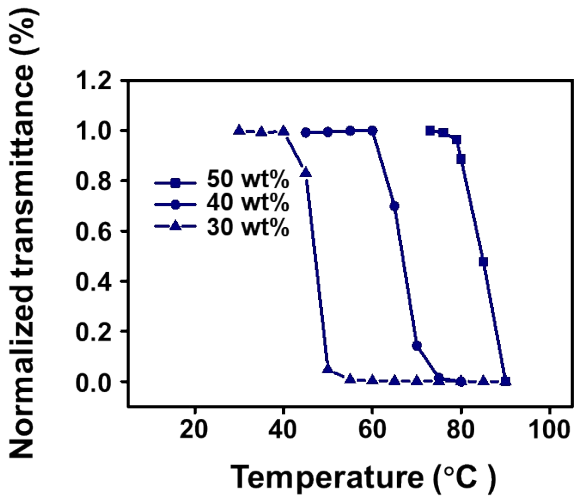

Figure S5. Temperature dependence of transmittance at 658 nm for 30 wt%, 40 wt% and 50 wt% PBA contents in PBA/[PrMIM][NTf_2] ionogels.

T_c was defined as the temperature at which the transmittance became 80 %. The PBA content increasing from 30 wt% to 50 wt%, T_c of corresponding ionogel increases from 47°C to 81°C.

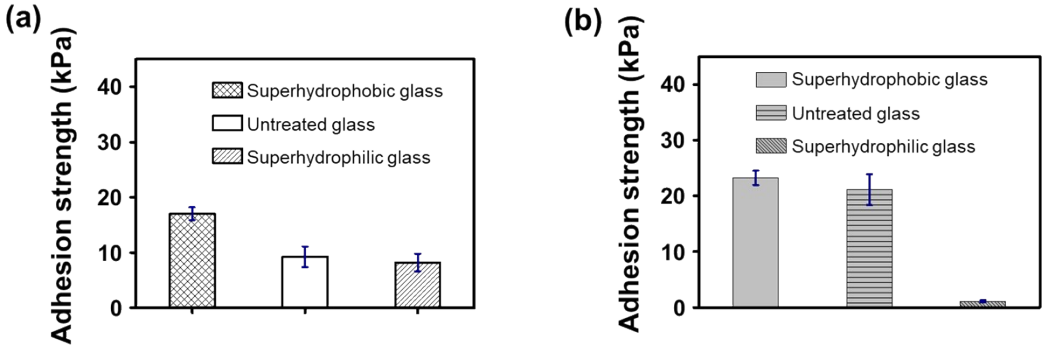

Figure S6. The adhesion strength of ionogels against untreated glass substrates, superhydrophobic and superhydrophilic glass substrates in air (a) and underwater (b).

The adhesion strength of ionogel against superhydrophilic glass substrates is lower than that of the other two substrates both in air and underwater. It is indicated that hydrophobicity of the substrates can effectively improve the strength of interfacial adhesion.

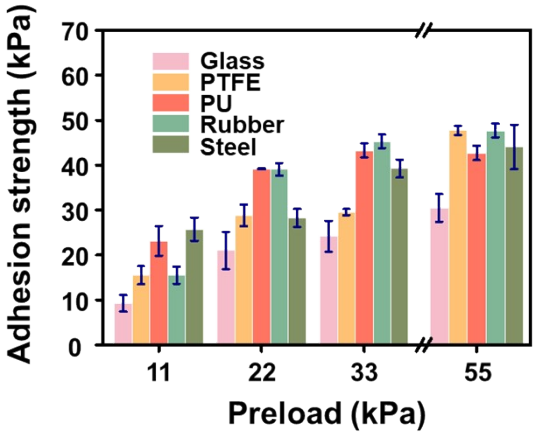

Figure S7. Adhesion strength of ionogels against various substrates under different preloads.

When the preload exceeds 33 kPa, the ionogels could form full contact with the substrates, and the adhesion strength reaches a plateau.

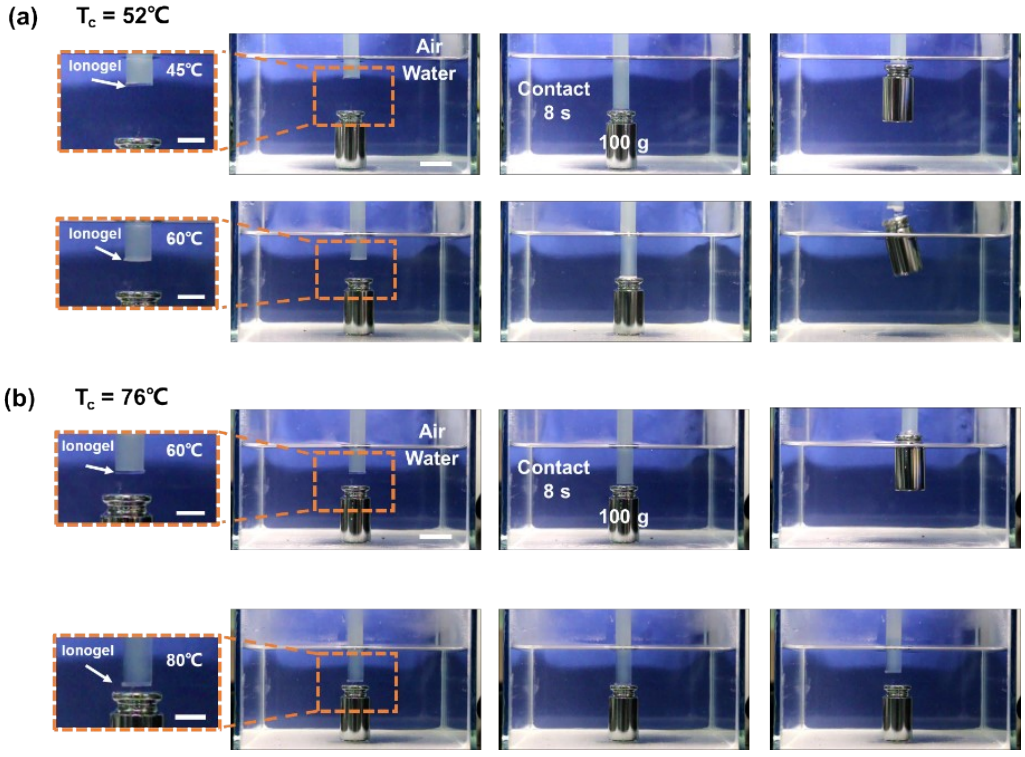

Figure S8. The demonstrations of the ionogels with different T_cs (52°C, 76°C) for capturing and releasing a heavy object (100 g) underwater at different temperatures.

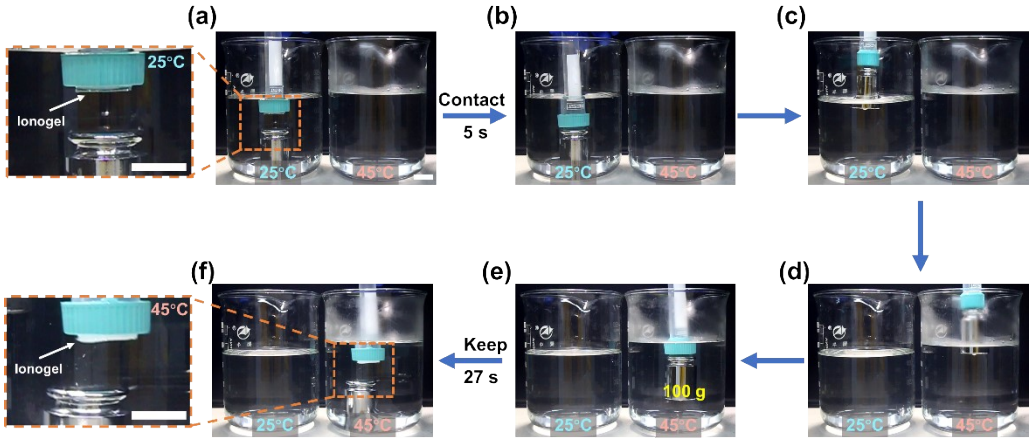

Figure S9. The demonstration of the ionogel ($T_c \sim 32°C$) for capturing and release a heavy object (100 g) underwater at different temperatures. (a) - (c) is the capturing process underwater at 25°C. (d) - (f) is the releasing process underwater at 45°C. Scale bar, 15 mm.

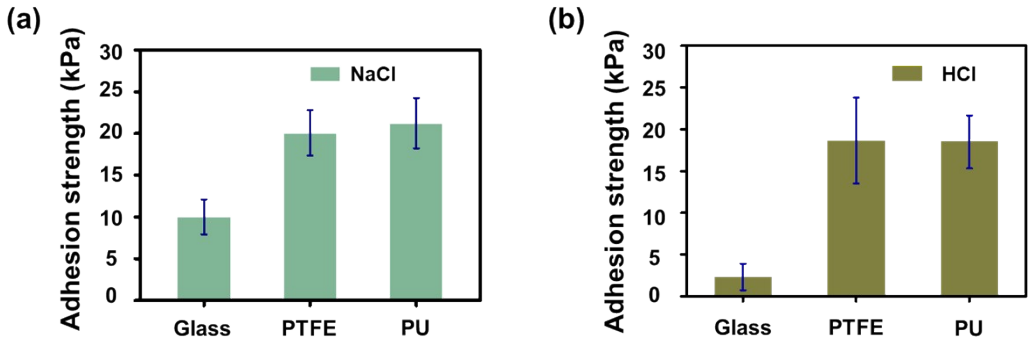

Figure S10. Adhesion strength of the ionogels against various substrates in different aqueous environments. (a) Adhesion strength of the ionogels in 1M NaCl solution. (b) Adhesion strength of the ionogels in 1M HCl solution.