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Electronic Supplementary Information

Fluorescent double network ionogel with fast self-healability and high resilience for reliable human motion detection

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Experimental section

Materials

Acrylamide (AM, 99%), 1,3,5-benzyltricarbaldehyde (BTC, 97%), N,N'-carbonyldiimidazole (CDI, 98%) and 2-hydroxy-2-methylpropiophenone (1173) were purchased from J&K Scientific Co., Ltd. Ionic liquid of 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) was purchased from Center for Green Chemistry and Catalysis (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). Agarose (AG, medium EEO, BC) was purchased from Sigma-Aldrich Trading Co., Ltd. Poly(ethylene glycol) diacrylate (PEGDA, average Mn = 508 g mol^{-1}) was purchased from Tianjing Jiuri Co., Ltd. All chemicals were used directly without purification.

Methods

Synthesis of AG-NH_2

Amino-modified agarose was synthesized through the reaction of AG with ethylenediamine *via* CDI activation method, as shown in Scheme S1. Firstly, AG was dissolved in anhydrous DMSO by heating and ten the solution was cooled to room temperature. The CDI was also dissolved in anhydrous DMSO and then added into the pre-dissolved AG solution. The already mixed solution was then stirred at room temperature for 2 hours. Excess ethylenediamine was added to the solution and stirred for 24 hours at room temperature under nitrogen. The obtained mixture was dialyzed with deionized water for 5 days using a dialysis membrane (MWCO: 8000−1400 Da). The final solid product of AG-NH_2 was obtained by freeze-drying, and was analyzed by fourier transform infrared spectroscopy (FI-IR, Fig. S2) and X-ray photoelectron spectroscopy (XPS, Fig. S3).

Preparation of ionogel

The ionogel was prepared by photopolymerization reaction of the precursor solution using the one-pot method. Firstly, AM as the polymerizable monomer, photoinitiator 1173 (1 wt% with respect to the mass of AM), crosslinker PEGDA (1 wt% with respect to the mass of AM), AG-NH_2 (1 wt% with respect to the mass of AM), [EMIM]Cl as well as the methanol solution containing BTC were added into the vial and stirred at 110 °C until being completely dissolved. The mass ratio of [EMIM]Cl to AM investigated in the work included 8:2, 7:3 and 6:4, and the mass ratio of BTC to AG-NH_2 was 0.05. Then, the clear precursor solution was immediately transferred into a poly(tetrafluoroethylene) mold and initiated under the UV light (365 nm) for 5 min to obtain the final ionogel.

Characterizations

Transparency test

The transparency of the ionogel was measured by UV spectrophotometer (UV-2450, SHIMADZU, Japan) in the visible region from 400 to 800 nm. The thickness of the sample was 1 mm.

Scanning electron microscopy (SEM) observation

Xerogel was obtained by solvent exchange method. The sample was first thoroughly immersed in constantly updated deionized water for 5 days to remove ILs, and then freeze dried under vacuum for 1 day. The sample was subjected to a gold spraying process, and observed by a scanning electron microscope (HITCHI SU 8010, Japan).

Fluorescence measurement

The fluorescence spectra of the ionogels were measured by the fluorescence spectrophotometer (Cary Eclipse, Varian, USA) at room temperature.

Optical microscopy observation

The self-healing process of the ionogel with crack were observed by optical microscope (Axio Scope A1, China). The self-healing efficiency of the ionogel was evaluated by the time it takes for the crack disappearing.

Fourier transform infrared spectroscopy (FT-IR)

Imine bonds formed in the ionogels were characterized by the fourier transform infrared spectrometer (TENSOR II, Bruker, Germany) operated in the range from 4000 to 400

cm^{-1}. The scanning rate was 32 cm s^{-1} and the resolution was 4 cm^{-1}.

Adhesion measurement

The ionogels were directly adhered to different materials for visual observation of adhesivity. The adhesive capacity was further studied through tensile adhesion test performed by universal testing machine (WDW-02, China). One piece of ionogel (2 cm × 2 cm) with a thickness of 5 mm was adhered to the overlapped parts of two pieces of staggered materials including glass, silica, paper and copper for testing.

Rheological measurement

Rheological properties of ionogels were analyzed by the rheometer (MCR 102, Anton Paar, Austria) at room temperature. The rheometer provides the gap of 1 mm and the parallel plate with a diameter of 25 mm. The oscillatory frequency during the stress sweep measurements was 10 rad s^{-1}. The angular frequency range of the frequency sweep was from 0.1 to 100 rad s^{-1}. In order to measure the viscosity of the ionogels, the steady-shear measurement was performed to assess the ionogel viscosity with a shear rate range of 0.001 to 10 s^{-1}.

Thermal analysis

Thermodynamic properties of ionogels were analyzed by differential scanning calorimeter (DSC 214, NETZSCH, Germany) and thermal gravimetric analyzer (TGA, DTG-60AH, SHIMADZU, Japan). The DSC measurements of ionogels were performed at a ramp rate of 10 K min^{-1} from −120 to 50 °C under flowing N_2. The TGA tests were carried out at a rate of 10 °C min^{-1} from 0 to 600 °C under flowing N_2.

Mechanical test

The mechanical properties of the ionogels were investigated by the universal testing machine (WDW-02, China). The samples used for tensile test were dumbbell shape with the size of 20 mm × 2 mm × 3 mm (length × width × thickness). The speed of tensile test was 50 mm min^{-1}. The sample for the compression test was a cylinder with a radius of 12 mm and a height of 6 mm. The speed of compression test was 10 mm min^{-1}.

Conductivity measurement

The ionic conductivities of the ionogel were measured by the alternating current impedance method using an electrochemical workstation (CHI660E, Shanghai Chenhua Instruments Co., Ltd.) equipped with a temperature controller. The sample was measured in a cell with a thickness of 1 mm and a radius of 4 mm, sandwiched between two pieces of ITO glasses. The measurements were performed in a frequency range from 10^6 to 0.1 Hz, under different temperatures. The ionic conductivity (σ) was calculated by the equation: $\sigma = L/(RS)$, where L is the thickness of the sample, R is the resistance obtained from the Nyquist plot, and S is the active area of the sample. Vogel-Tamman-Fulcher (VTF) equation is $\sigma T^{1/2} = A \exp[-B/(T-T_0)]$, where A represents pre-exponential factor in connection with the number of ion carriers, B represents the activation energy of ion transport, and T_0 represents the ideal glass transition temperature.

Sensing performance test

The strain sensors were assembled with the ionogel as the ionic conductor. Attributed to the excellent self-adhesion, they could be adhered directly to different joints of human body including fingers, wrists, elbows and knees to trace human actions, without any other assistance of adhesive tapes. A robotic palm attached with the ionogel was used to complete sensing tests in extreme temperatures. The real-time resistance (*R*) of the ionogel sensor under different strains was calculated by the *I-t* curve, which was measured by the electrochemical workstation at a constant voltage of 2 V. The relative resistance change ($\Delta R/R_0$) was calculated from the equation: $\Delta R/R_0 = (R - R_0) / R_0 \times 100\%$, where R_0 is the initial resistance without strain. The gauge factor (GF) was defined according to the formula: $GF = (\Delta R/R_0)/\varepsilon$, where ε was the applied tensile strain.

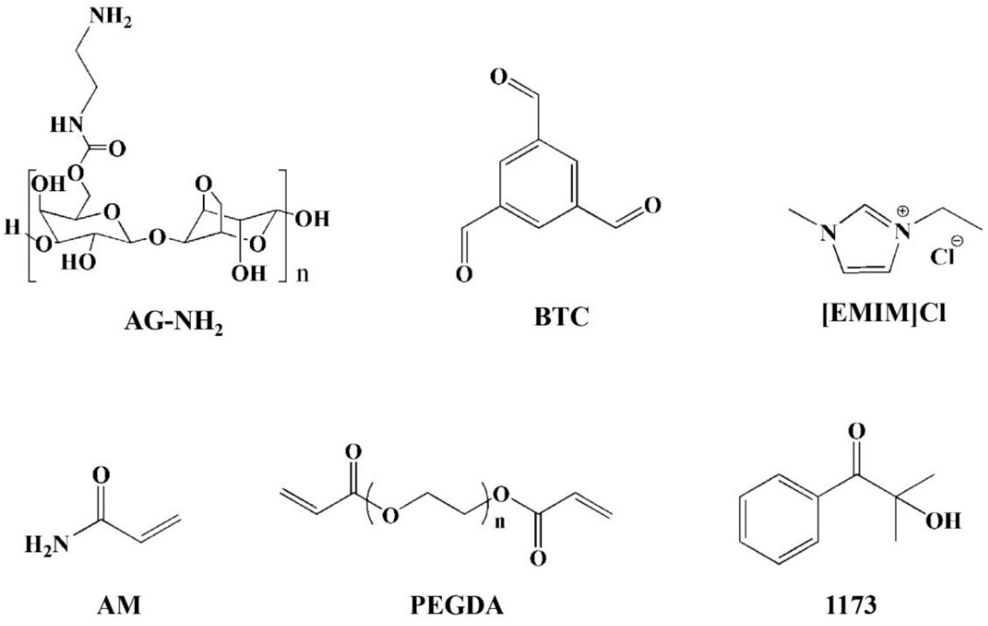
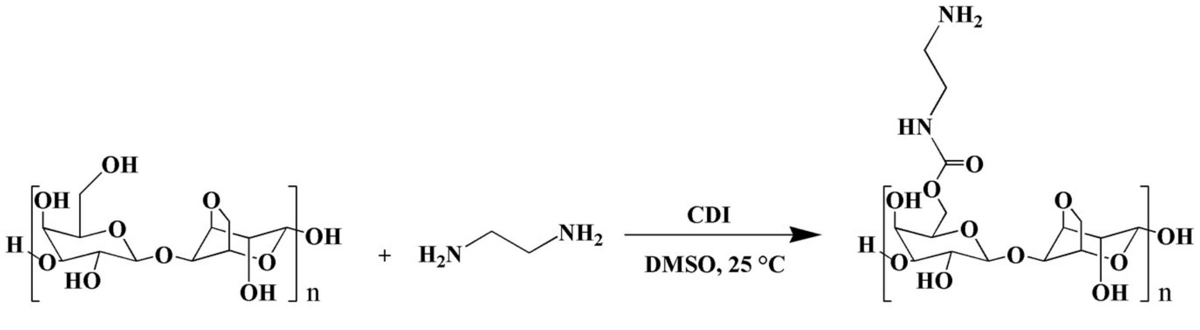


Fig. S1 Chemical structures.



Scheme S1. Synthetic route of amino-modified agarose (AG-NH_2).

Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) have been measured to confirm the successful synthesis of AG-NH_2 by introducing amino groups to agarose skeleton. As shown in Fig. S2, compared to FT-IR spectrum of AG, the appearance of several new characteristic bands indicates the introduction of amino groups. The characteristic bands at 1703, 1256 and 767 cm^{-1} for AG-NH_2 can be assigned to stretching vibration of C=O, stretching vibration of C–N and bending vibration of N–H, respectively. The N 1s peak of XPS spectrum comprising two components is shown in Fig. S3. The peaks at 399.2 eV and 400.0 eV can be assigned to –NH– and –NH_2, respectively. The above results confirm the preparation of amino-group functionalized agarose.

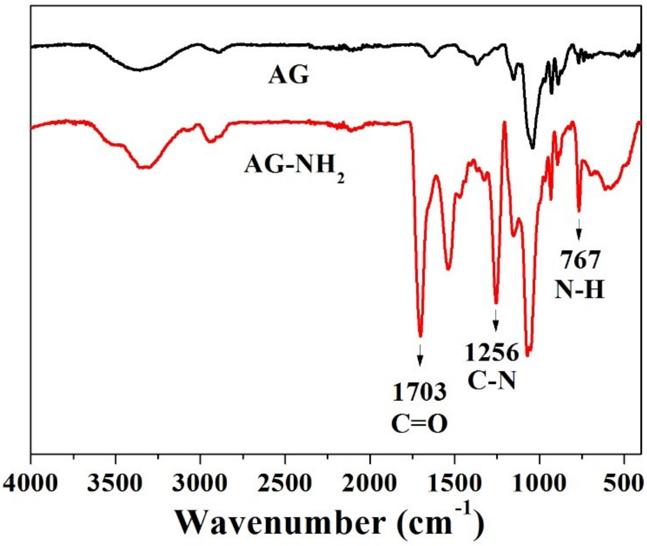


Fig. S2 FT-IR spectra of AG and AG-NH_2.

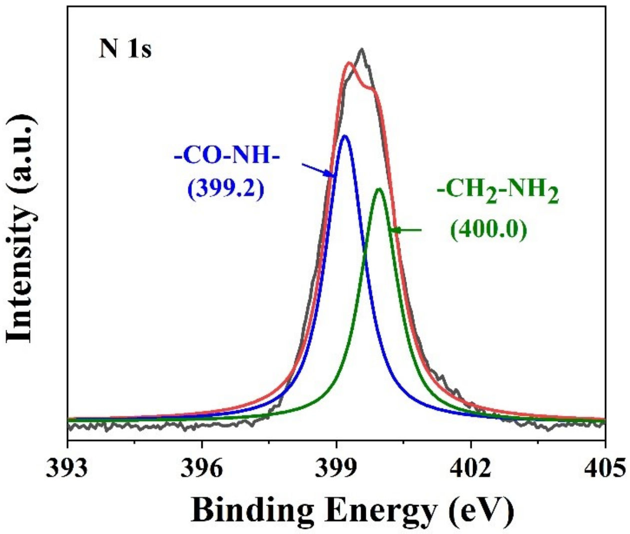


Fig. S3 N 1s spectra of AG-NH_2.

Fig. S4 (a) Photograph of the ionogel without BTC under UV light and (b) observation obtained from the fluorescence microscope.

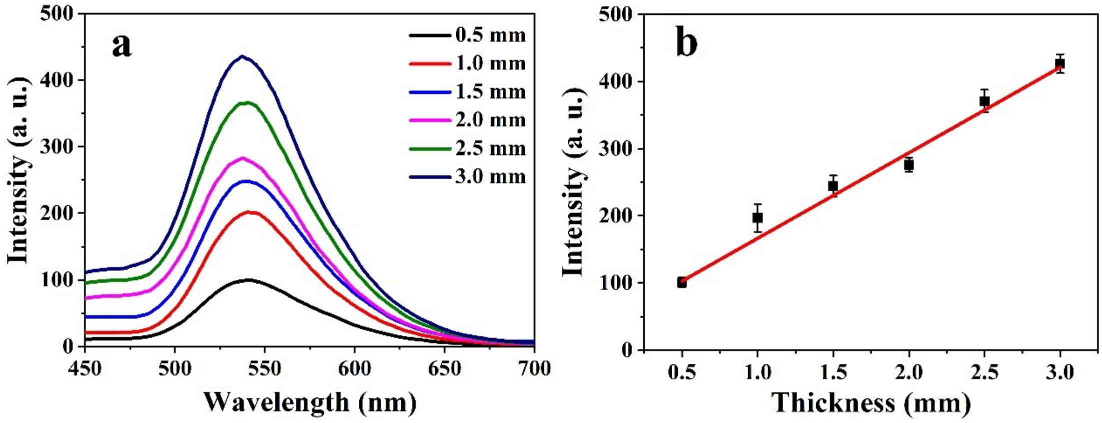


Fig. S5 (a) Fluorescence emission spectra for ionogels with different thicknesses at the excitation wavelength of 365 nm. The mass ratios of [EMIM]Cl to AM for all ionogels are 8:2. (b) Fluorescence intensity at 533 nm versus the thickness of ionogels.

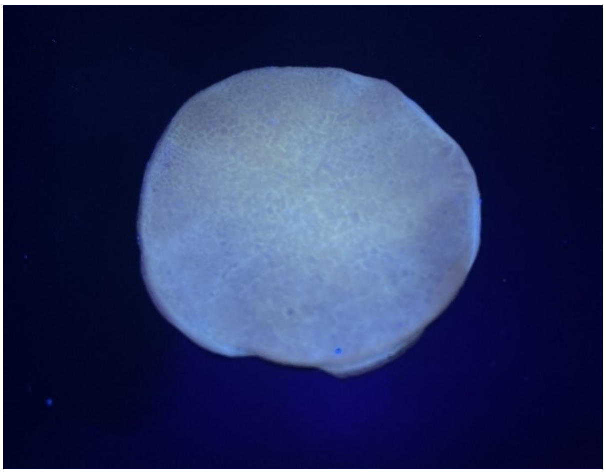


Fig. S6 Photograph of xerogel under UV light.

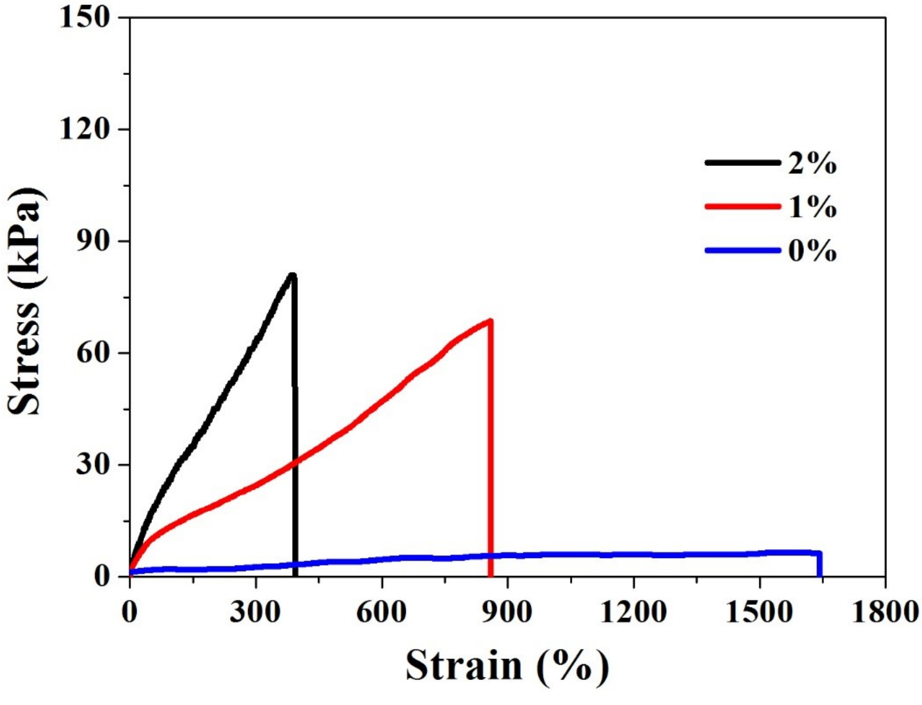


Fig. S7 Tensile stress-strain curves of ionogels with different PEGDA concentrations.

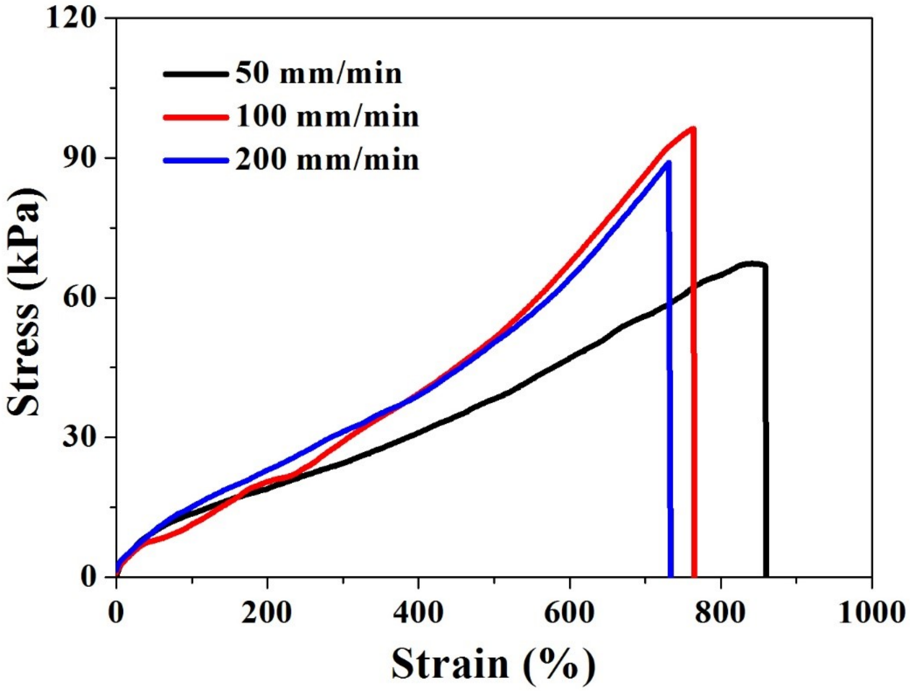


Fig. S8 Tensile stress-strain curves of ionogels at different stretching rates.

In order to evaluate the mechanical stability of the ionogels exposed to ambient moisture for a long time, tensile stress-strain measurements were performed. As shown in Fig. S9, three samples have been tested, including fresh ionogel and two ionogels which have been placed in the ambient conditions for 3 days (RH ≈ 46%) and about 8 months, respectively. Compared to the fresh sample, the values of fracture stress and strain for the other two ionogels decreased slightly. Obviously, even after 8 months, the fracture stress and strain of the ionogel decreased to a small degree, verifying its excellent mechanical stability.

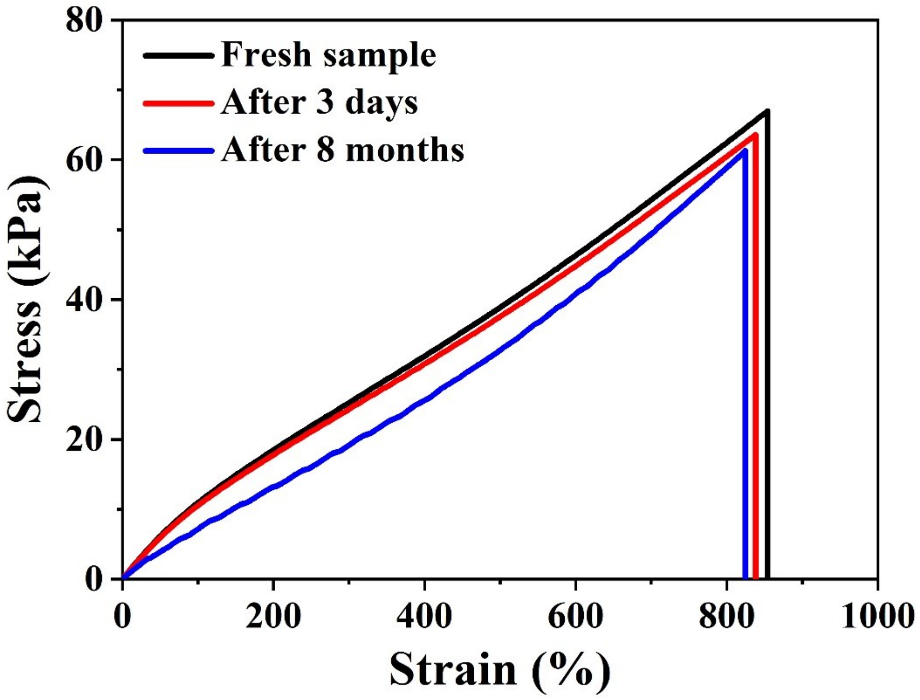


Fig. S9 Tensile stress-strain curves of different ionogels.

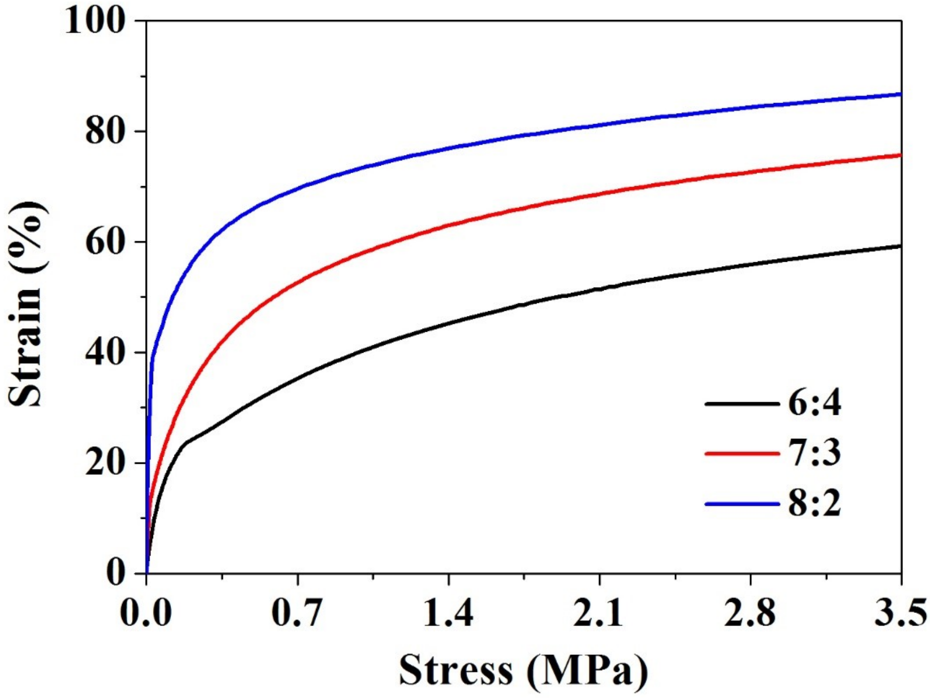


Fig. S10 Compressive stress-strain curves of the ionogels with [EMIM]Cl and AM mass ratios ranging from 8:2 to 6:4.