Supplementary information

Multi-crosslinked strong, tough and anti-freezing organohydrogels for flexible sensors

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Supplementary Figures

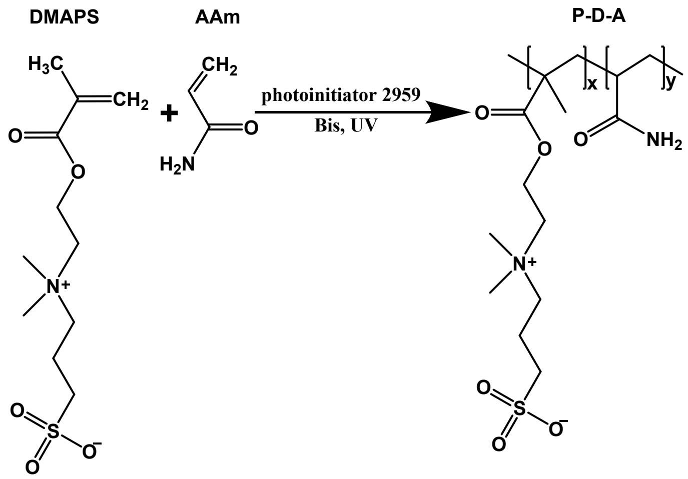

Fig. S1 Chemical structure schematic illustration of the reaction process to synthesize the PDA block copolymer.

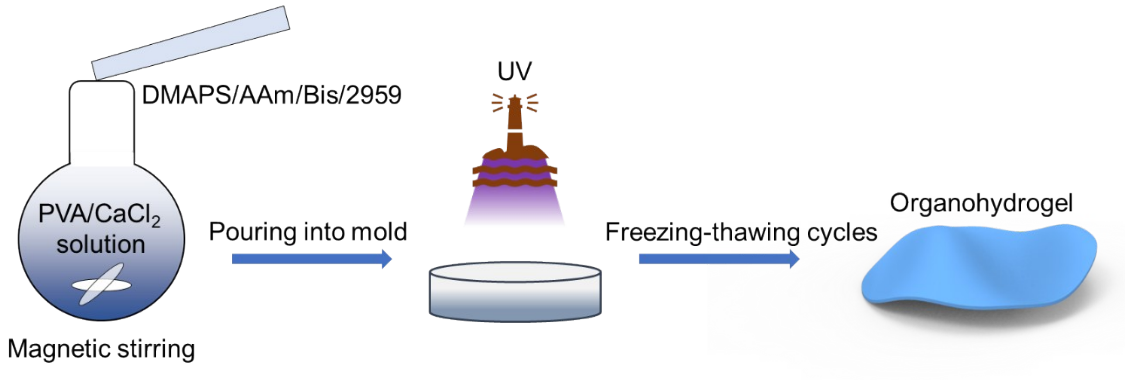

Fig. S2 Fabrication process of the organohydrogel.

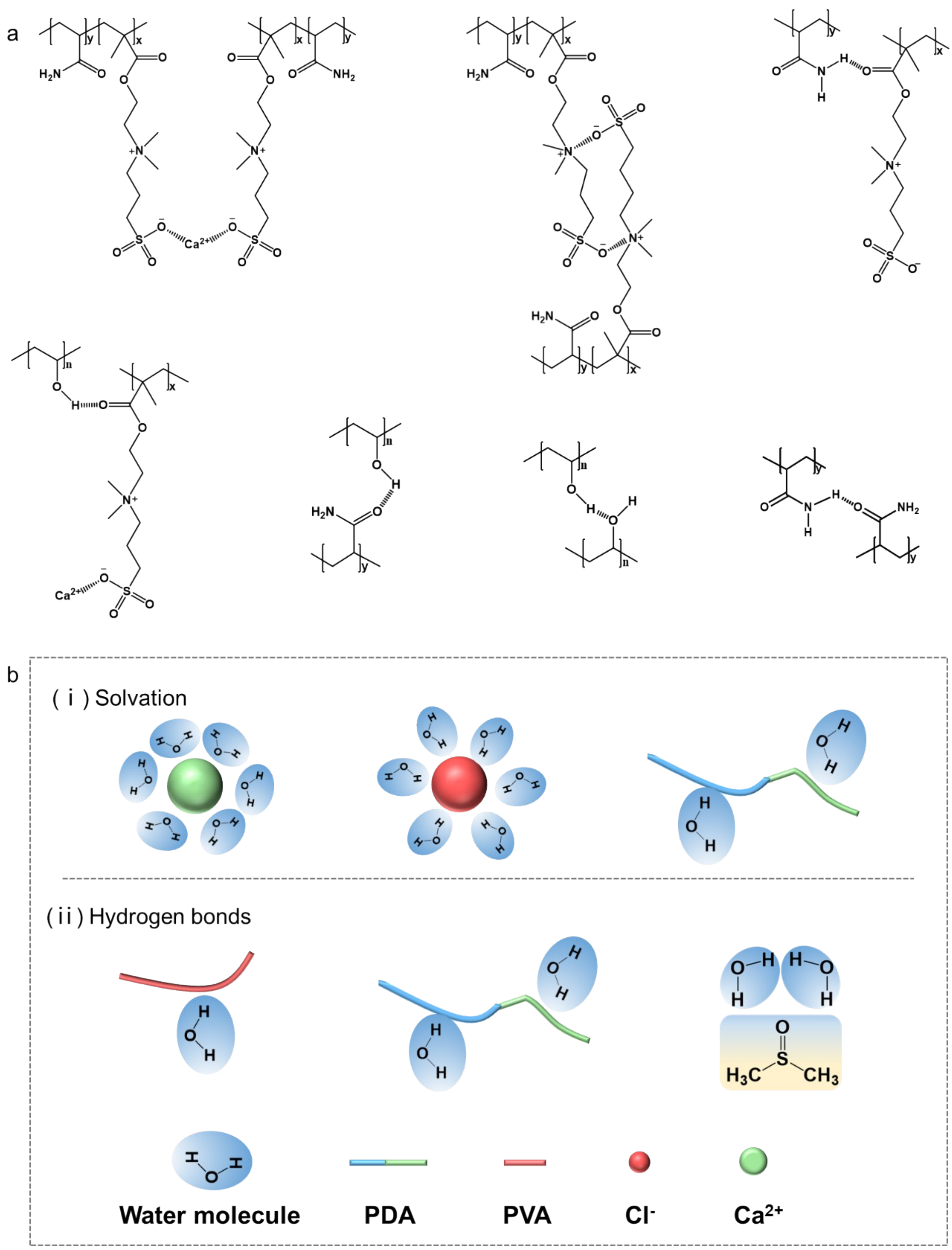

Fig. S3 (a) Crucial chemical bonds of the organohydrogel. (b) Interactions between the water molecules and the other components.

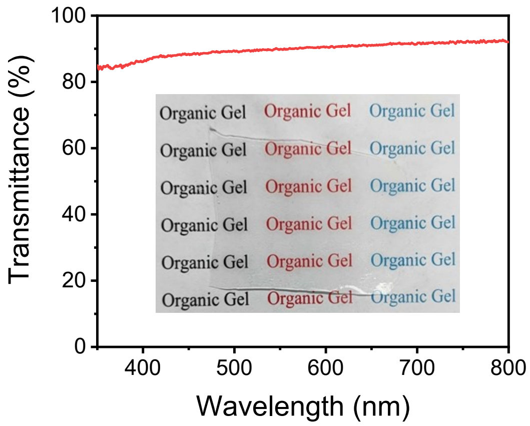

Fig. S4 UV-vis transmittance of the organohydrogel. The insert picture is the digital photograph of the organohydrogel.

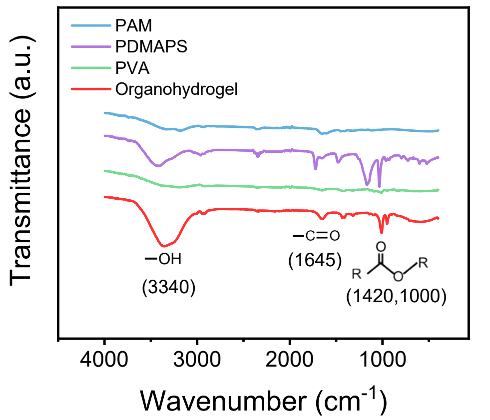

Fig. S5 Fourier transform infrared (FT-IR) spectra of the PAM, PDMAPS, PVA hydrogels, and the organohydrogel.

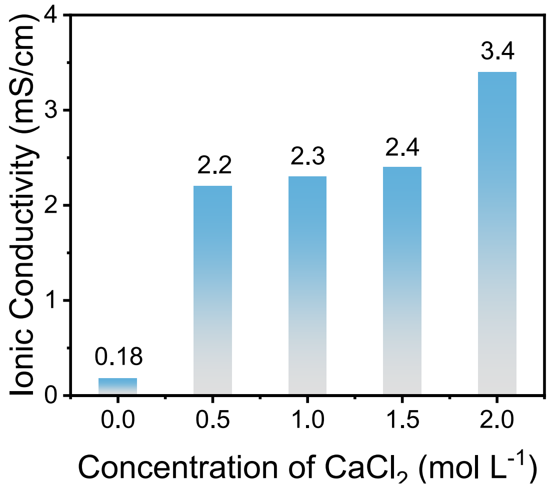

Fig. S6 Ionic conductivities of the organohydrogels with the different $CaCl_2$ concentrations.

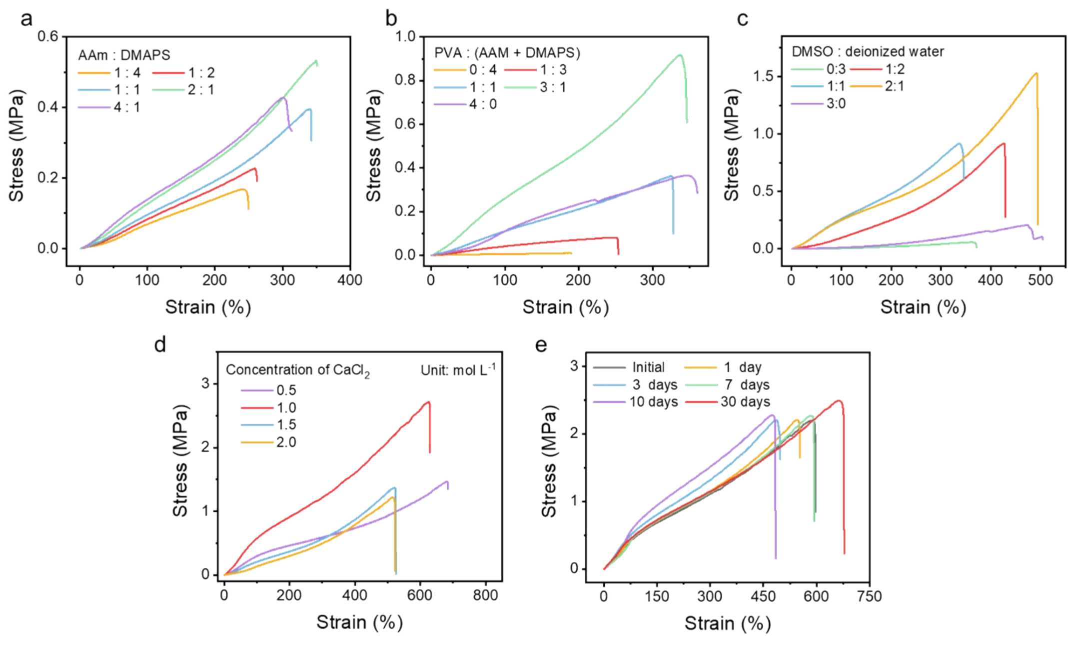

Fig. S7 Stress-strain curves of the organohydrogels with the mass ratios of (a) AAm: DMAPS= 1:4, 1:2, 1:1, 2:1, and 4:1. (b) PVA: (AMM+DMAPS)= 0:4, 1:3, 1:1, 3:1, and 4:0. (c) DMSO: deionized water= 1:2, 1:1, and 2:1. (d) Stress-strain curves of the organohydrogels with the $CaCl_2$ concentrations of 0.5 M, 1.0 M, 1.5 M, and 2.0 M. (e) Stress-strain curves of the organohydrogels which are deposited in ambience for 1 day to 30 days.

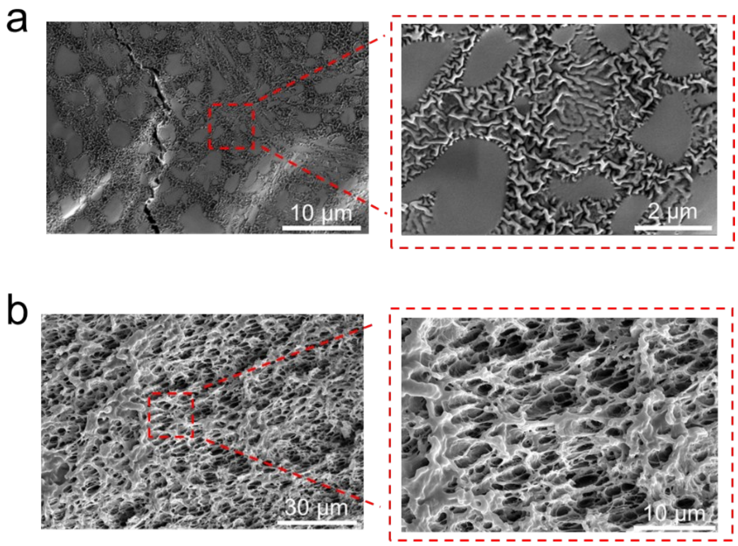

Fig. S8 SEM images of (a) the organohydrogel and (b) the PVA hydrogel.

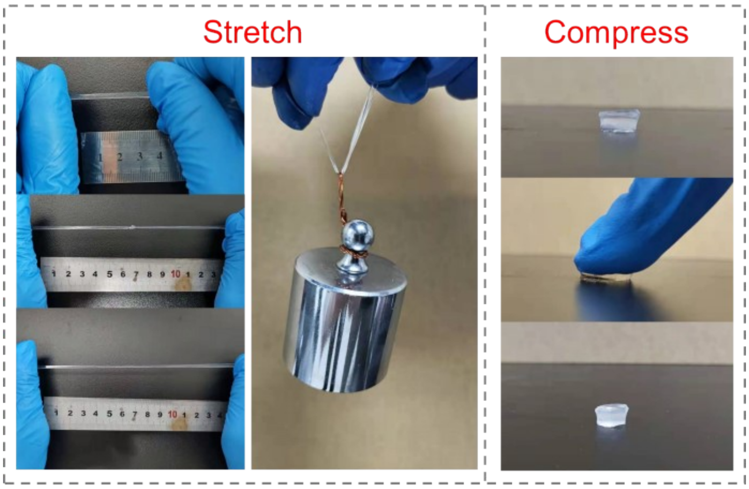

Fig. S9 Photographs of the organohydrogels with or without knot as being stretched to 3 times the initial length, holding a 500 g weights, and compressed by human's finger.

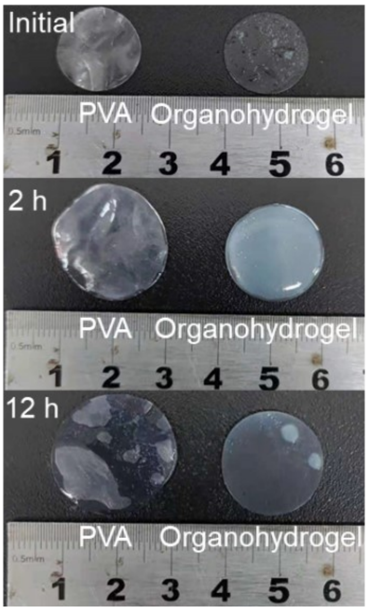

Fig. S10 Digital photographs of the PVA hydrogel and the organohydrogel which are swelled in the deionized water for 0 h, 2 h, and 12 h.

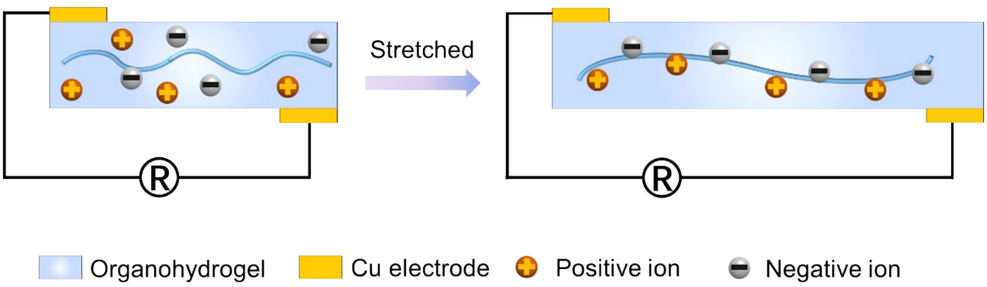

Fig. S11 Ion distribution of the resistive mode sensor as being stretched or not.

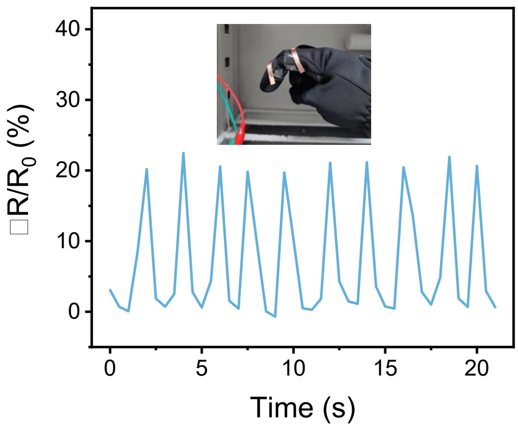

Fig. S12 Resistive variation of the strain sensor as the human's finger is bended to 90º at sub-zero temperature (-20℃).

Supplementary Tables

Table S1. The contents of all gel components.

Gels \ Weight	Monomer	Solvent	Inorganic salt	Initiator	Cross-linking agent
PVA hydrogel	PVA (1.5 g)	DIW (10 g)	—	—	—
PAM hydrogel	AAm (1.5 g)	DIW (10 g)	—	2959 (7.5 mg)	Bis (7.5 mg)
PDMAPS hydrogel	DMAPS (1.5 g)	DIW (10 g)	—	2959 (7.5 mg)	Bis (7.5 mg)
organohydrogel	PVA (0.75 g) DMAPS (0.08 g) AAm (0.17 g)	DIW (2.22 g) DMSO (4.44 g)	$CaCl_2$ (0.74 g)	2959 (2.5 mg)	Bis (1.3 mg)

DIW: Deionized water

Bis: N,N'-Methylenebisacrylamide

2959: Photo-initiator 2959

Table S2. Fracture energy andfracture strength of some reported gels.

Gels	Fracture energy (J m^{-2})	Fracture strength (MPa)
This work	6.84	2.74
PAM-peptibe-Zn^{2+}	1.35	0.56
P(NaSS-co-MPTC)	4	2.6
PAMPS-PAAm	4.4	2
PS-DN	2.67	1.6
Agar/HPAM	1	0.267
NPs-P-PAA	5.5	0.11
PDA-pGO-PAM	6.78	0.17
P-DN(PAMPS/PAM)	3	0.47
Ionogel	4.7	1

Table S3. Full titles of the different materials.

Abbreviation	Full title
PE	Polyethylene
PTFE	Polytetrafluoroethylene
PI	Polyimide
PET	Polyethylene terephthalate

Supplementary Notes

Note S1. Computational process of the mechanical strength and toughness.

Mechanical strength:

According to the formula of $\sigma = \frac{F}{S}$, for the normal stress σ_0, S_0 is the original cross-sectional area of the sample strip. But for the true stress σ_T, S_T is real-time cross-sectional area, which is decreasing as the sample is being stretched. Assuming the sample volume is constant during the tensile text, the S_T can be calculated as $S_T = \frac{S_0}{\varepsilon + 1}$, where, ε is the strain. So,

$$the\ true\ stress\ \sigma_T = \frac{F}{S_0} \times (\varepsilon + 1) = \sigma_0 \times (\varepsilon + 1)$$

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Toughness:

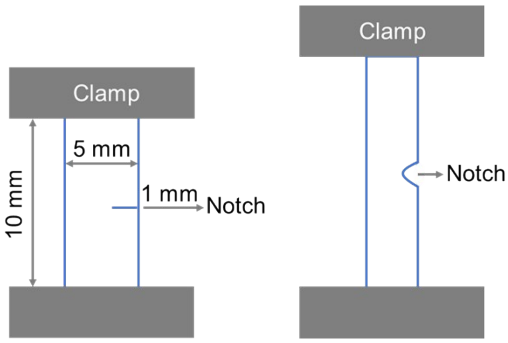

Fig. S13 Schematic illustration of the single-edge notched elastomer used for determining the fracture energy.

According to the methodology reported in the literatures,[1,2] the fracture toughness of the organohydrogel can be expressed as:

$$G_c = \frac{6Wc}{\sqrt{\lambda_c}}$$

where λ_c is (breaking strain +1) of the notched sample, c is length of the notch. W is the energy which is calculated by integrating the stress versus strain of the un-notched samples until λ_c (shaded area in Fig. 3h). The sample was notched in single-edge, and the stretching speed is 3 mm min^{-1}.

References

[1] H. W. Greensmith, Rupture of rubber. X. The change in stored energy on making a small cut in a test piece held in simple extension. *J. Appl. Polym. Sci.* **1963**, *7*, 993-1002.

[2] Wang, X., Zhan, S., Lu, Z., Li, J., Yang, X., Qiao, Y., Men, Y., Sun, J., Healable, Recyclable, and Mechanically Tough Polyurethane Elastomers with Exceptional Damage Tolerance. *Adv. Mater.* **2020**, 32, 2005759.