Supporting Information

Thermal-driven H-bond reconfiguration for bioinspired high-strength anisotropic supramolecular hydrogels

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Supporting Methods

Synthesis of NASC monomer

The synthesis method of the NASC monomer is the same as that previously reported[1, 2]. Dissolve aminourea hydrochloride (31.75 g) in 30 mL of deionized (DI) water, followed by 168 mL of cold K_2CO_3 solution (2 M) and 90 mL of cold ether in a 500 mL round-bottom flask. Subsequently, 28.50 g of acryloyl chloride in 120 mL of ether was added dropwise to the mixture with stirring at 0°C for about 4 hours. The resulting white precipitate is filtered and washed with cold water to obtain a crude product. The crude product was then dissolved in DI water and stirred at 95 °C for 1 h. After that, the undissolved pellet is removed by centrifugation and the supernatant is lyophilized to obtain the final NASC monomer.

Preparation of PNAGA hydrogel

25 wt% of NAGA monomer was dissolved in deionized water, and Lithium Phenyl(2,4,6-trimethylbenzoyl) phosphinate (LAP, 0.5 wt% of the total mass of the monomer) was added as a photoinitiator. The mixture was irradiated under ultraviolet light for 2 minutes until completely cured to obtain PNAGA hydrogel.

Quenching process of the PNAGA hydrogel

Hydrogel samples are clamped in a custom-made stretching unit equipped with a servo-motor drive system and pre-stretched in deionized water at 50 °C. The strain ratio (6 times the initial length) is systematically programmed via a digital control panel. Immediately after the hydrogel reaches the target elongation, it is quenched in deionized water at 0 °C for 2 minutes to reconstruct the fixed-oriented structure using fast hydrogen bonding. Finally, the quenched hydrogel was transferred to deionized water at 25 °C for equilibration for 7 days to obtain the quenched PNAGA hydrogel.

Supporting Discussion

Chemical structure characterization

Fourier-transform infrared spectroscopy (TFS-66 V/S, Bruker, Germany) of the NASC monomer precursor (**Figure S1**) revealed diagnostic absorption bands at: 3439 (NH), 3332 (NH), 3219 (NH), 3062 (NH), 1683 (C=O), 1623 (C=C), 1594 (NH); **Figure S2 and Figure S3** present the NMR spectra of the NASC monomer. The corresponding positions have been clearly marked in the figures. In the ^{1}H NMR spectrum, the chemical shifts are observed at $\delta =$ 9.8 (H_a), 7.9 (H_b), 6.2 (H_c), 6.0 (H_d), and 5.7 (H_e). Similarly, in the ^{13}C NMR spectrum, the signals appear at $\delta =$ 164.7 (C_a, -CO-), 159.0 (C_b, -CO-), 130.2 (CH_2-CH-), and 126.6 (CH_2-CH-). These results confirm the successful synthesis of the NASC monomer.

Performance analysis of PNA hydrogels with different monomer contents.

The mechanical analysis of PNA hydrogels with different monomer concentrations revealed a clear trend: as the monomer content increased, the tensile strength at break gradually improved, rising from 3.9 ± 0.4 MPa for PNA_{20} to 9.5 ± 0.4 MPa for PNA_{40} (**Figure S4-S5**). Similarly, the Young's modulus increased from 2.5 ± 0.2 MPa to 5.9 ± 0.2 MPa (**Figure S6**). Notably, the elongation at break first increased and then decreased with higher monomer content, reaching a maximum of 981.4 ± 61.8 % for PNA_{25}. Considering the balance between elongation and strength, PNA_{25} was selected for quenching due to its optimal mechanical properties. This hydrogel exhibited the highest toughness, reaching 32.6 ± 5.4 MJ/m³ (**Figure S7**).
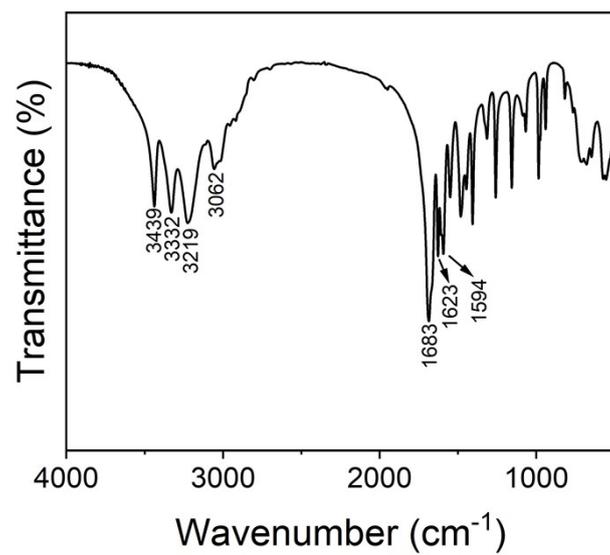
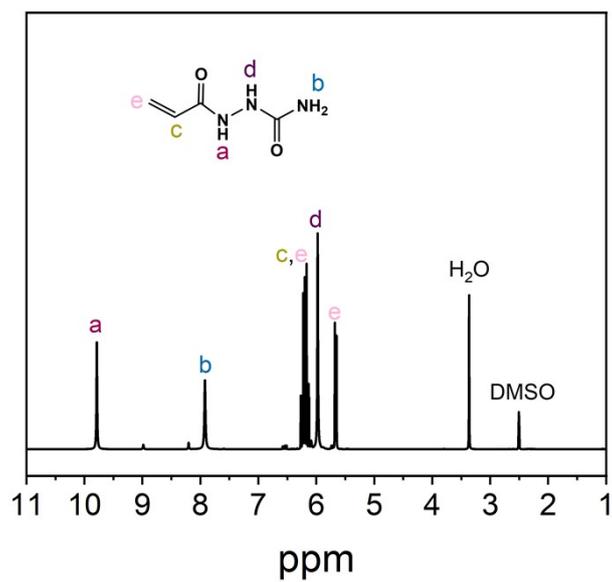**Figure S1.** FTIR spectra of the NASC monomer.

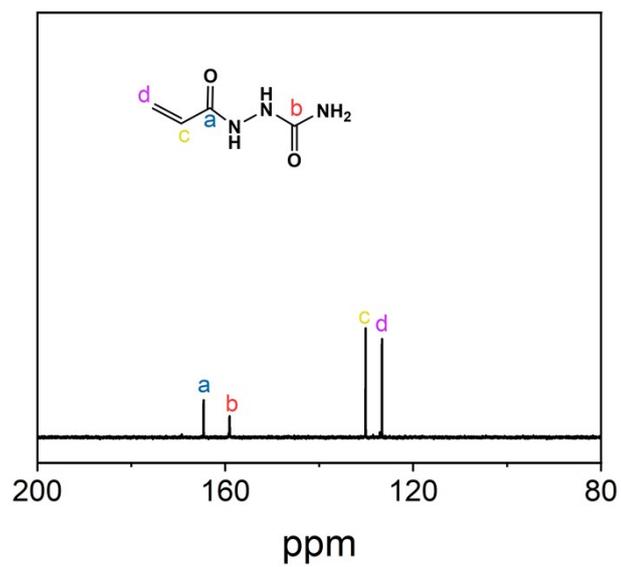**Figure S2.** ^{1}H NMR spectra of the NASC monomer.

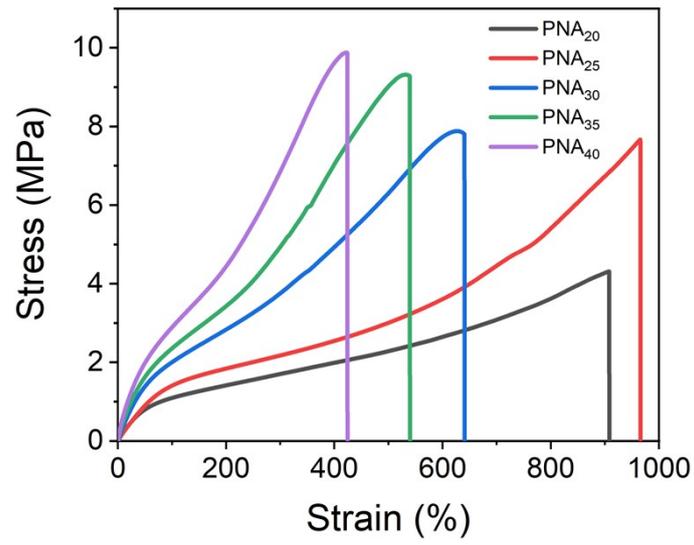**Figure S3.** ^{13}C NMR spectra of NASC monomer.

Figure S4. Stress-strain curves of PNA hydrogels with different monomer contents.
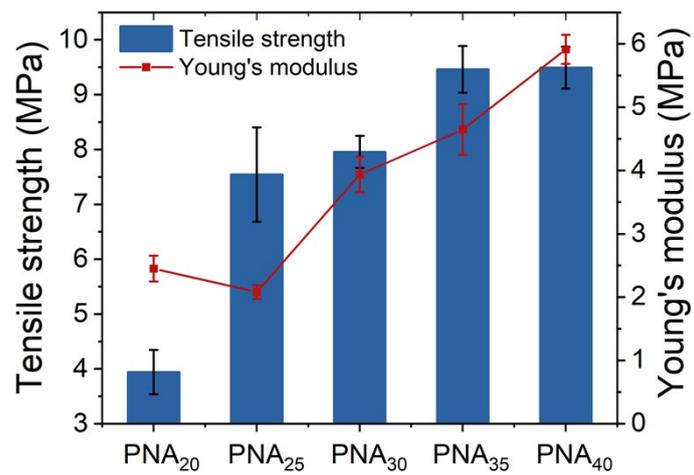
Figure S5. Tensile strength and Young's modulus of PNA hydrogels with different monomer contents. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.
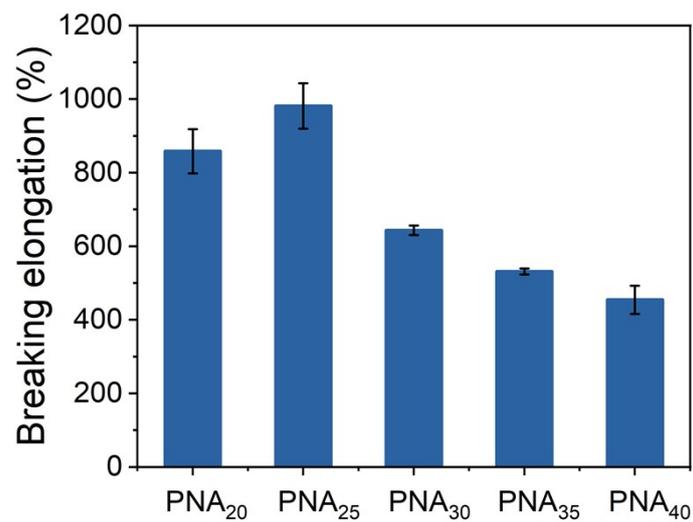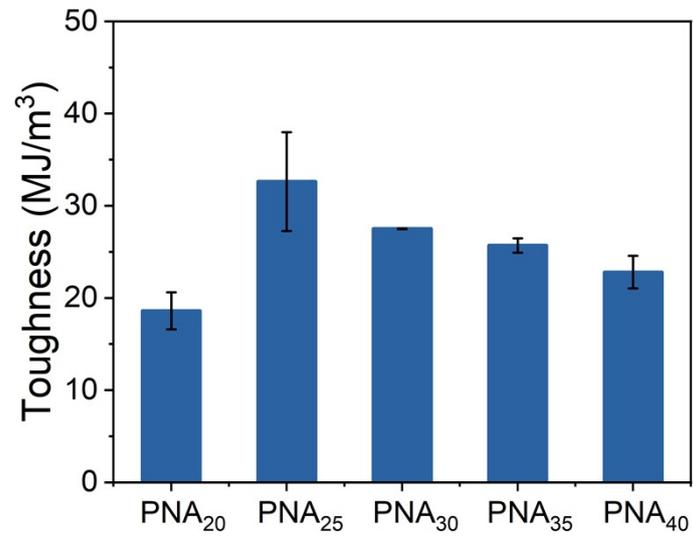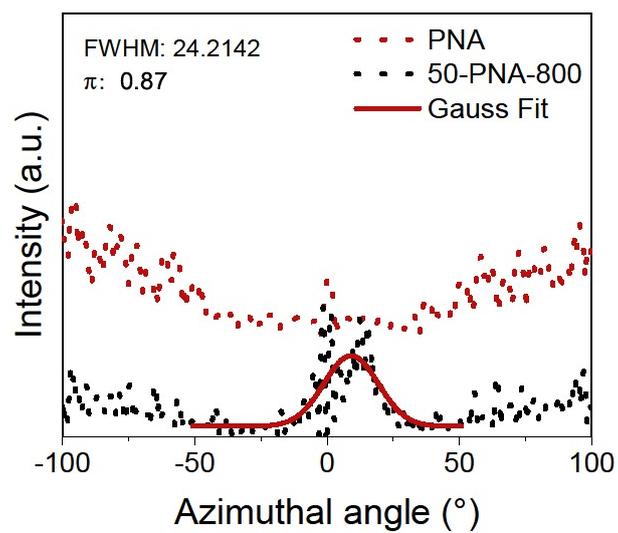
Figure S6. Tensile elongation at break of PNA hydrogels with different monomer contents. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.

Figure S7. Toughness of PNA hydrogels with different monomer contents. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.

Figure S8. 2D SAXS patterns' corresponding azimuthal angle plots of the hydrogel.
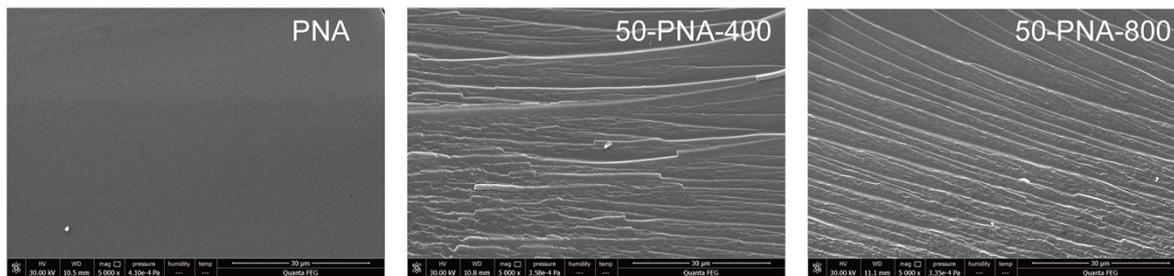
Figure S9. The SEM image of PNA, 50-PNA-400 and 50-PNA-800.
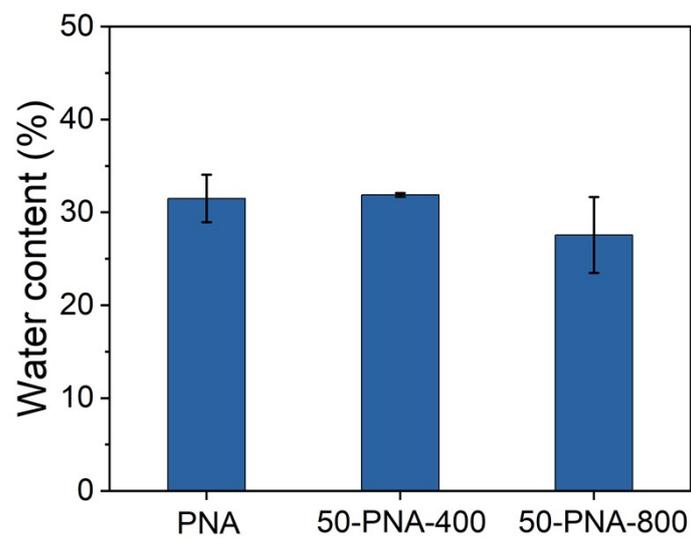
Figure S10. The water content of the pristine PNA, 50-PNA-400 and 50-PNA-800. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.
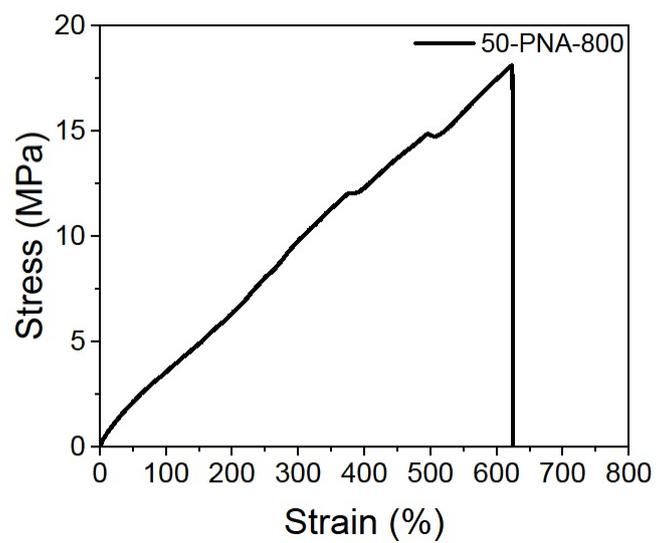
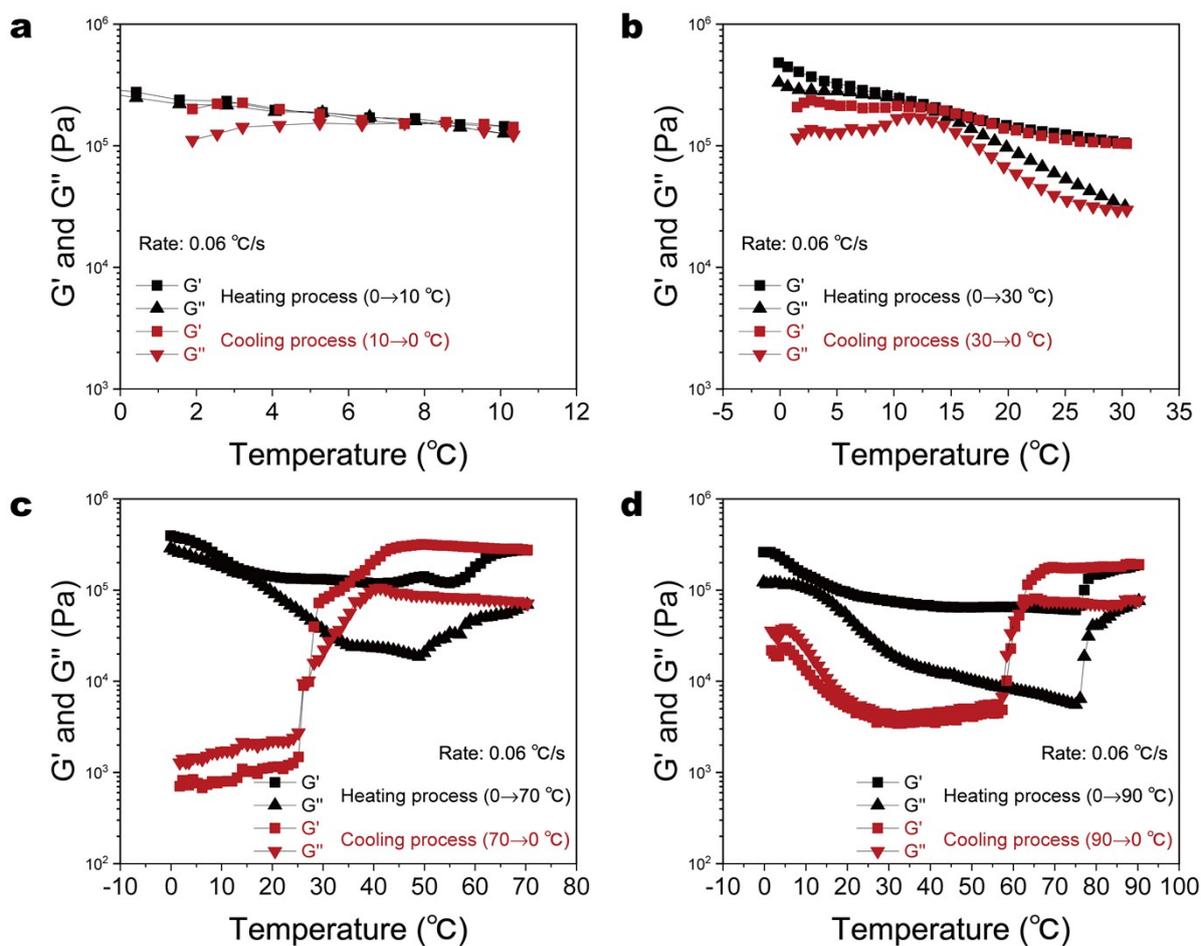**Figure S11.** Stress-strain curves of 50-PNA-800 hydrogels after 14 days of immersion in water post-quenching.

Figure S12. (a) Rheological test of PNA hydrogel from 0 °C to 10 °C and back from 10 °C to 0 °C. (b) Rheological test of PNA hydrogel from 0 °C to 30 °C and back from 30 °C to 0 °C. (c) Rheological test of PNA hydrogel from 0 °C to 70 °C and back from 70 °C to 0 °C. (d) Rheological test of PNA hydrogel from 0 °C to 90 °C and back from 90 °C to 0 °C. The frequency of 1 Hz and a strain is 1%.
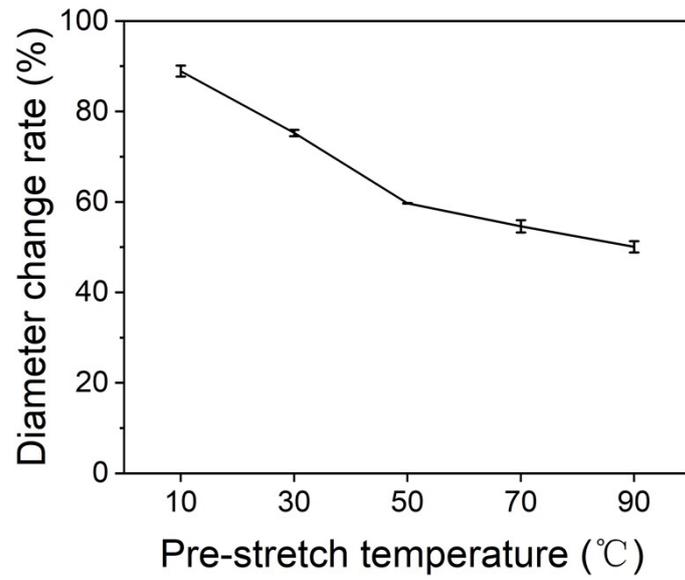
Figure S13. The diameter changes rate of hydrogels quenched after being stretched to 800% at different temperatures at 7 days. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.
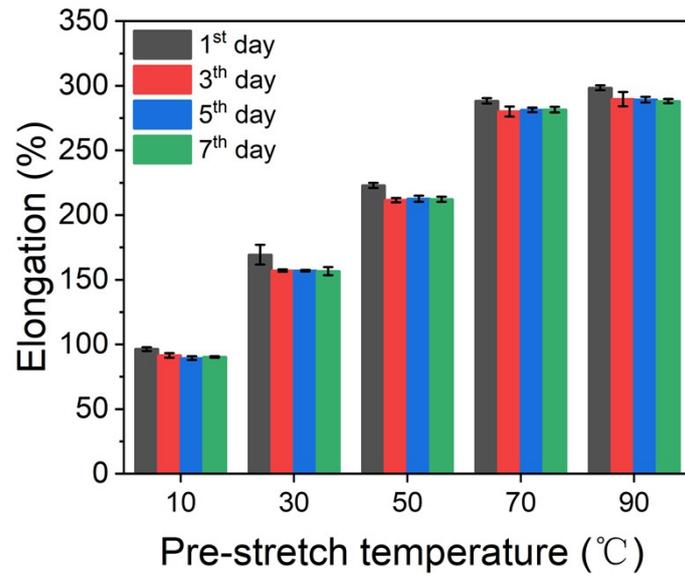
Figure S14. The elongation of hydrogels quenched after being stretched to 800% at different temperatures at 1 day to 7 days. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.
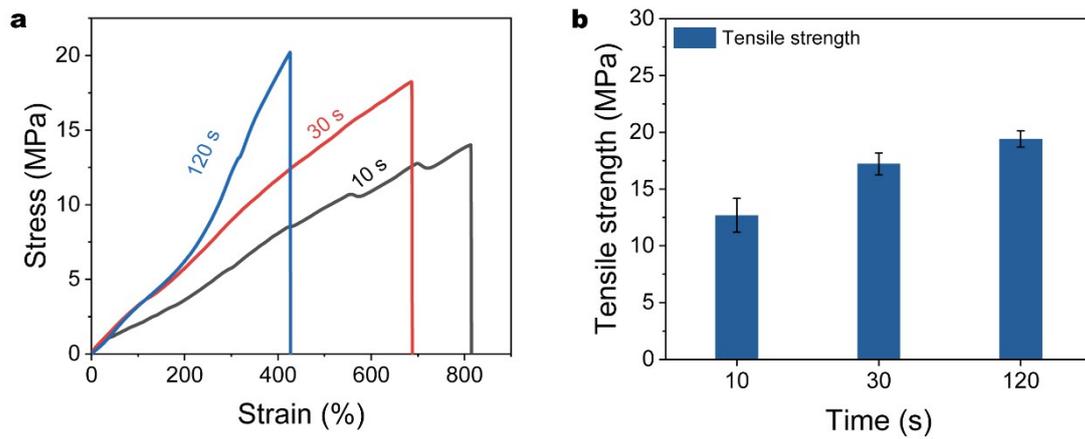
Figure S15. (a) Stress-strain curves and corresponding (b) tensile strength of 50-PNA-800 hydrogels quenched in 0 ℃ water under different time. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.
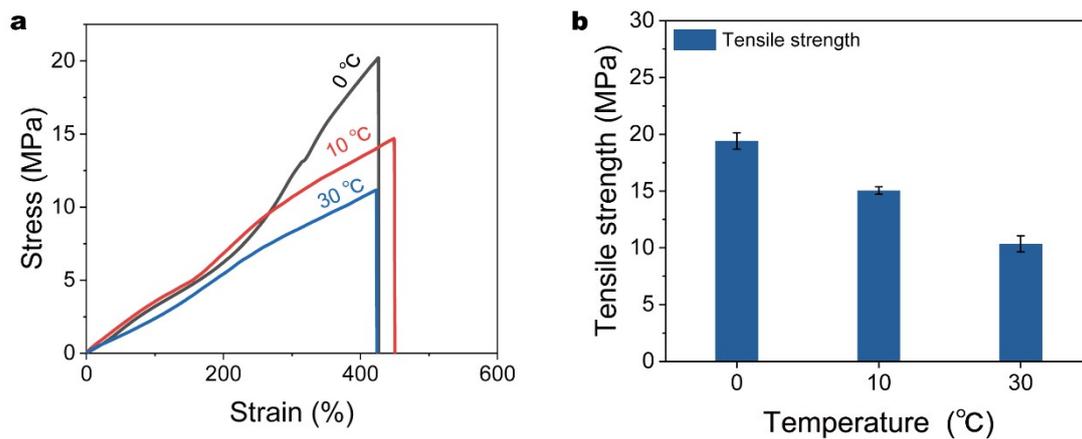
Figure S16. (a) Stress-strain curves and corresponding (b) tensile strength of 50-PNA-800 hydrogels quenched in water at different temperatures for 2 minutes. Error bars represent the standard deviation (n = 3). The data is presented as mean values ± SD.
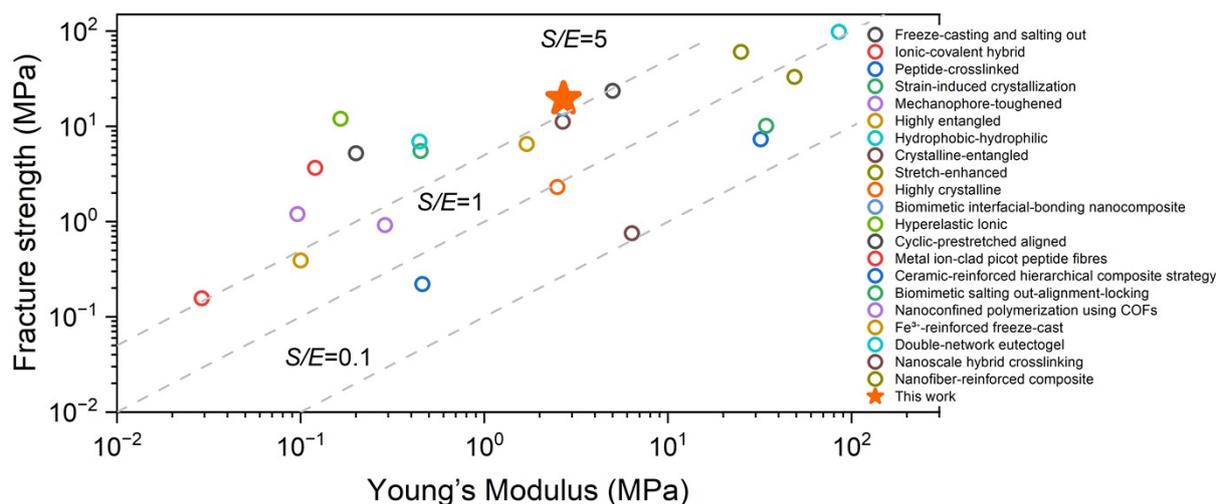
Figure S17. Comparison chart in the Ashby plot of Young's modulus versus fracture strength of quenched hydrogel with other reported strong and tough hydrogel. These hydrogels types include freeze-casting and salting out,[3] ionic-covalent hybrid,[4] peptide-crosslinked,[5] strain-induced crystallization,[6] mechanophore-toughened,[7] highly entangled,[8] hydrophobic-hydrophilic,[9] crystalline-entangled,[10] stretch-enhanced,[11] highly crystalline,[12] biomimetic interfacial-bonding nanocomposite,[13] hyperelastic ionic[14] cyclic-prestretched aligned,[15] metal ion-clad picot peptide fibres,[16] ceramic-reinforced hierarchical composite strategy,[17] biomimetic salting out-alignment-locking,[18] nanoconfined polymerization using COFs,[19] Fe^{3+}-reinforced freeze-cast,[20] double-network eutectogel,[21] nanoscale hybrid crosslinking,[22] nanofiber-reinforced composite.[23]
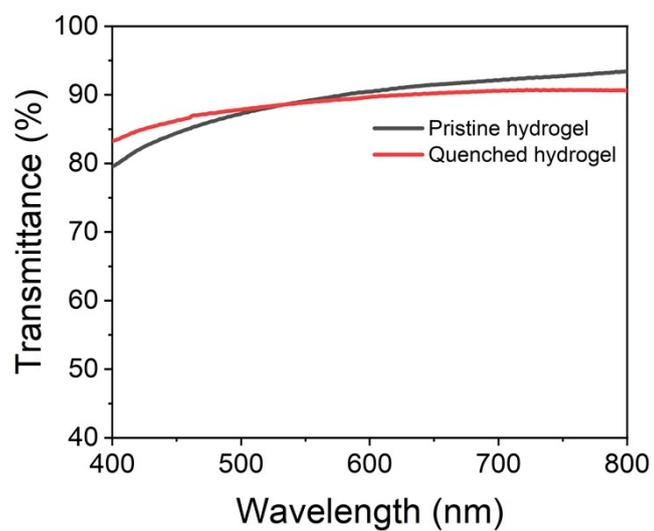
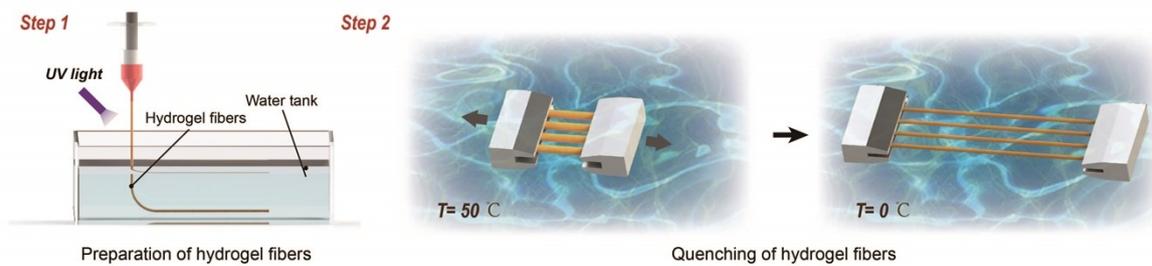**Figure S18.** The transmittance of the pristine and quenched hydrogel (50-PNA-800).

Figure S19. Schematic diagram of hydrogel fiber extrusion, pre-stretching and quenching process.
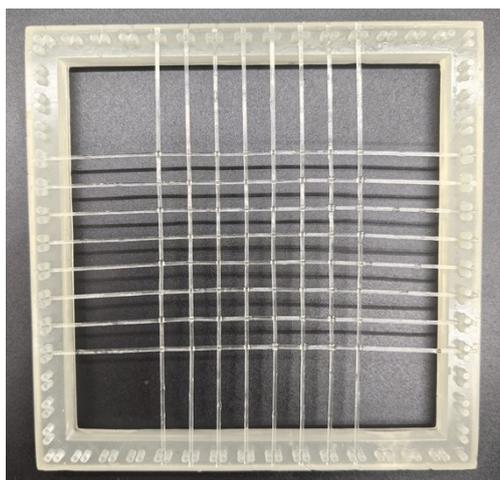
Figure S20. Drop-weight impact test of the hydrogel fiber mesh. The dimensions of the outer frame are 10 cm × 10 cm.

References

1. C. Fan, B. Liu, Z. Xu, C. Cui, T. Wu, Y. Yang, D. Zhang, M. Xiao, Z. Zhang and W. Liu, *Mate. Horiz.*, 2020, **7**, 1160-1170.
2. J. Wu, Y. Wang, P. Jiang, X. Wang, X. Jia and F. Zhou, *Nat. Commun.*, 2024, **15**, 3482.
3. M. Hua, S. Wu, Y. Ma, Y. Zhao, Z. Chen, I. Frenkel, J. Strzalka, H. Zhou, X. Zhu and X. He, *Nature*, 2021, **590**, 594-599.
4. J. Y. Sun, X. Zhao, W. R. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. Suo, *Nature*, 2012, **489**, 133-136.
5. P. Liu, Y. Zhang, Y. Guan and Y. Zhang, *Adv. Mater.*, 2023, **35**, e2210021.
6. C. Liu, N. Morimoto, L. Jiang, S. Kawahara, T. Noritomi, H. Yokoyama, K. Mayumi and K. Ito, *Science*, 2021, **372**, 1078-1081.
7. Z. Wang, X. J. Zheng, T. Ouchi, T. B. Kouznetsova, H. K. Beech, S. Av-Ron, T. Matsuda, B. H. Bowser, S. Wang, J. A. Johnson, J. A. Kalow, B. D. Olsen, J. P. Gong, M. Rubinstein and S. L. Craig, *Science*, 2021, **374**, 193-196.
8. J. Kim, G. G. Zhang, M. X. Shi and Z. G. Suo, *Science*, 2021, **374**, 212-+.
9. G. G. Zhang, J. Steck, J. Kim, C. H. Ahn and Z. G. Suo, *Sci. Adv.*, 2023, **9**.
10. Y. Wu, Y. Zhang, H. Wu, J. Wen, S. Zhang, W. Xing, H. Zhang, H. Xue, J. Gao and Y. Mai, *Adv. Mater.*, 2023, **35**, e2210624.
11. X. Wang, S. Zheng, J. Xiong, Z. Liu, Q. Li, W. Li and F. Yan, *Adv. Mater.*, 2024, **36**, e2313845.
12. S. T. Lin, X. Y. Liu, J. Liu, H. Yuk, H. C. Loh, G. A. Parada, C. Settens, J. Song, A. Masic, G. H. McKinley and X. H. Zhao, *Sci. Adv.*, 2019, **5**.
13. B. Bao, Q. Zeng, K. Li, J. Wen, Y. Zhang, Y. Zheng, R. Zhou, C. Shi, T. Chen, C. Xiao, B. Chen, T. Wang, K. Yu, Y. Sun, Q. Lin, Y. He, S. Tu and L. Zhu, *Nat. Mater.*, 2023, **22**, 1253-1260.
14. L. L. Chen, Z. K. Jin, W. W. Feng, L. Sun, H. Xu and C. Wang, *Science*, 2024, **383**, 1455-1461.
15. S. Lin, J. Liu, X. Liu and X. Zhao, *Proc. Natl. Acad. Sci. U.S.A.*, 2019, **116**, 10244-10249.
16. B. Xue, Z. Bashir, Y. Guo, W. Yu, W. Sun, Y. Li, Y. Zhang, M. Qin, W. Wang and Y. Cao, *Nat. Commun.*, 2023, **14**, 2583.
17. Q. Liu, X. Dong, H. Qi, H. Zhang, T. Li, Y. Zhao, G. Li and W. Zhai, *Nat. Commun.*, 2024, **15**, 3237.
18. X. Sun, Y. Mao, Z. Yu, P. Yang and F. Jiang, *Adv. Mater.*, 2024, **36**, e2400084.
19. W. Li, X. Wang, Z. Liu, X. Zou, Z. Shen, D. Liu, L. Li, Y. Guo and F. Yan, *Nat. Mater.*, 2024, **23**, 131-138.
20. X. Guo, X. Y. Dong, G. J. Zou, H. J. Gao and W. Zhai, *Sci. Adv.*, 2023, **9**.
21. C. Xu, A. Xie, H. Hu, Z. Wang, Y. Feng, D. Wang and W. Liu, *Nat. Commun.*, 2025, **16**, 2589.
22. S. Lin, C. Cao, Q. Wang, M. Gonzalez, J. E. Dolbow and X. Zhao, *Soft Matter*, 2014, **10**, 7519-7527.
23. H. Zhuo, X. Dong, Q. Liu, L. Hong, Z. Zhang, S. Long and W. Zhai, *Nat. Commun.*, 2025, **16**, 980.

Video S1. Comparative tensile behavior of the pristine versus unquenched hydrogels

Video S2. Drop-weight impact test of the hydrogel fiber meshs