Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information for

Supramolecular topology controlled self-healing conformal hydrogels for stable human-machine interfaces

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1. Synthesis of 9-(2-bromoethyl)-9H-purin-6-amine

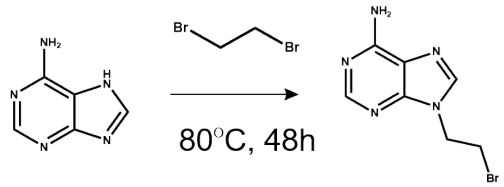

Figure S1. Synthetic route of 9-(2-bromoethyl) adenine (A-Br).

A mixture of adenine (2.5 g, 18.5 mmol), dibromoethane (8.6 mL, 80.73 mmol) and potassium carbonate (5.11 g, 37 mmol) in ultra-dry DMF (100 mL) was stirred at 80°C for 48 h under N_2 atmosphere. Then the mixture was filtered to remove unreacted adenine, the excess dibromoethane and DMF were distilled off under reduced pressure to obtain the product A-Br as light-yellow solid. Yield: 75%. ESI-MS (*m/z*): $[M+H]^+$ calcd. for $C_7H_8BrN_5$: 241.9963; found: 242.0072. The ^1H NMR spectrum is shown in Figure S2, and the mass spectrum result is shown in Figure S3.

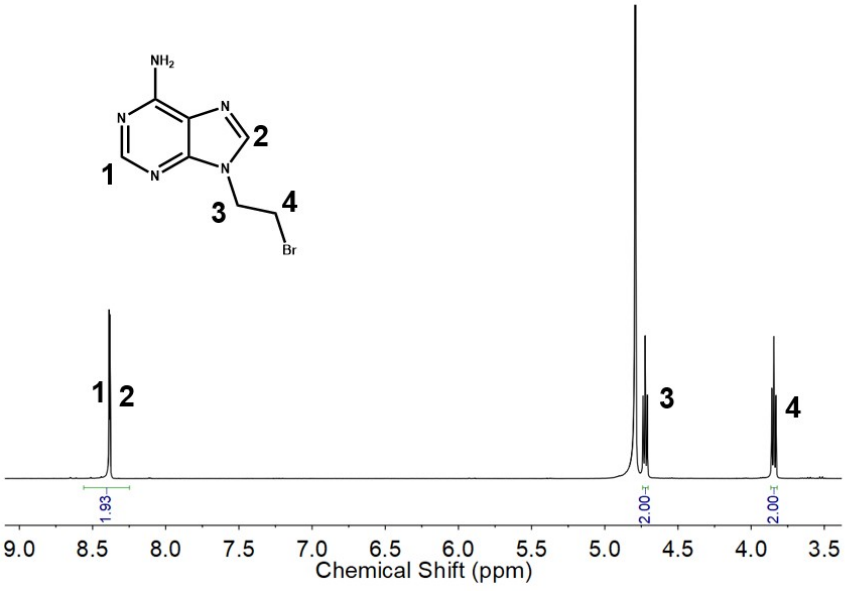

Figure S2. ^1H NMR (400 MHz) spectrum of A-Br in D_2O.

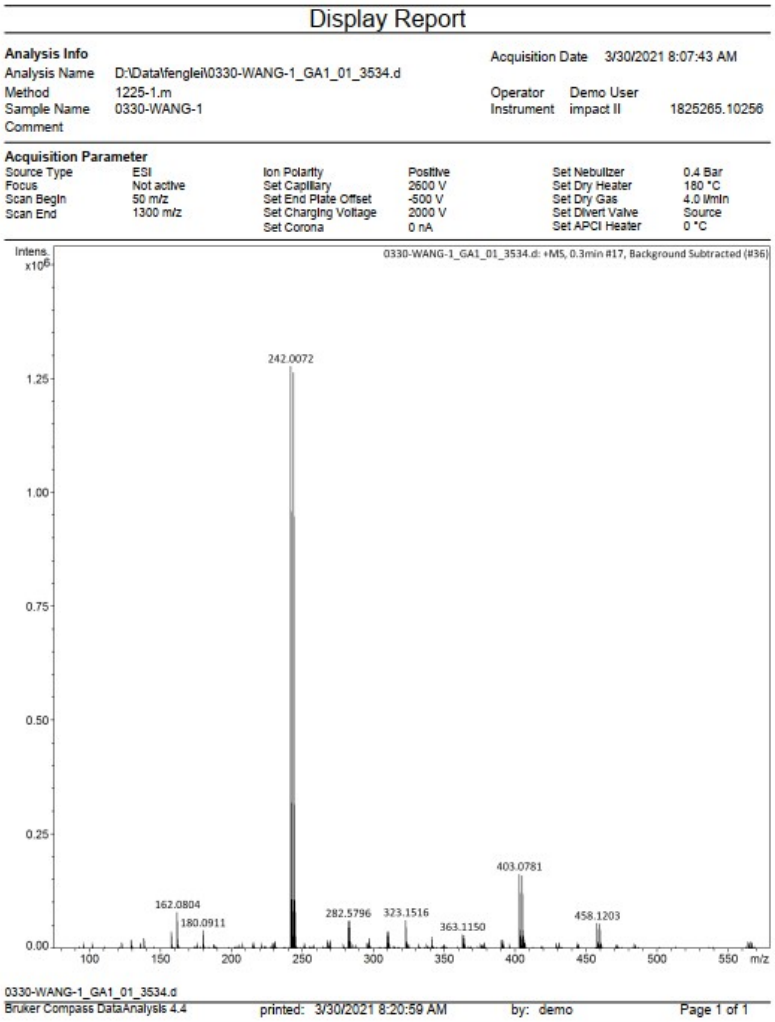

Figure S3. ESI mass spectrum of A-Br.

2. Synthesis of ADMAPAA

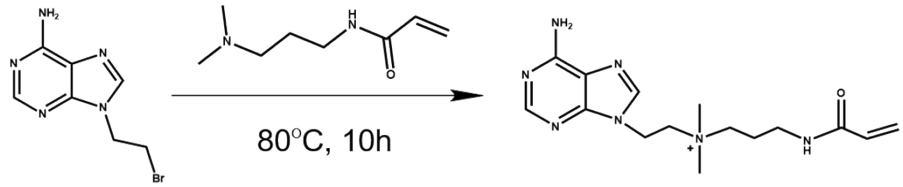

Figure S4. Synthetic route of ADMAPAA.

A mixture of A-Br (1.5 g, 6.2 mmol) and N,N-dimethylpropylacrylamide (1.45 g, 9.68 mmol) in ultra-dry DMF (10 mL) was stirred at 80°C for 10 h under N_2 atmosphere.

Dissolution-precipitation operations with methanol and ether were operated to purify the crude product precipitated by ether, then dried under vacuum to obtain the product ADMAPAA as brown viscous solid. Yield: 65%. ESI-MS (*m/z*): $[M\text{-}Br]^+$ calcd. for $C_{15}H_{24}N_7O^+$: 318.2037; found: 318.2076. The ^1H NMR spectrum is shown in Figure S5, and the mass spectrum result is shown in Figure S6.

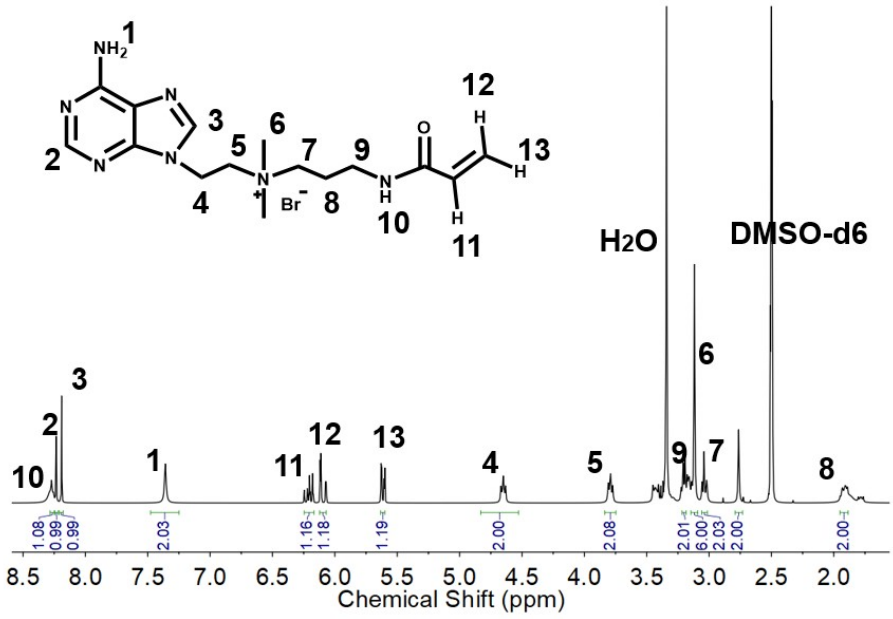

Figure S5. ^1H NMR (400 MHz) spectrum of ADMAPAA in DMSO-d6.

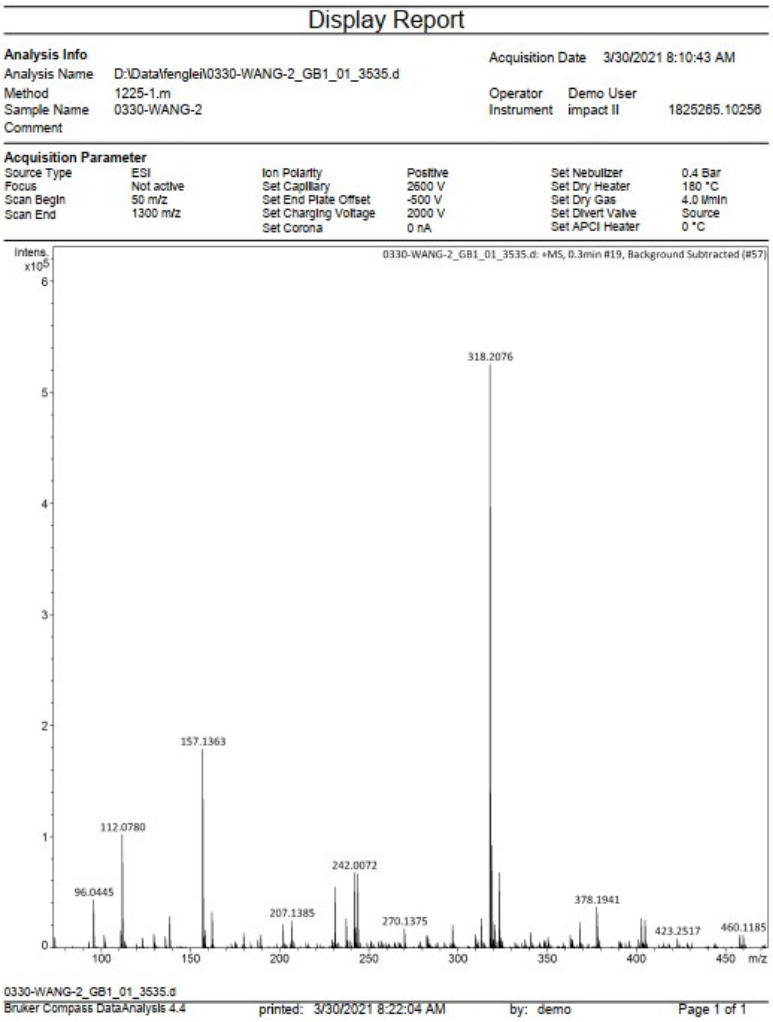

Figure S6. ESI mass spectrum of ADMAPAA.

3. Synthesis of CDMAPAA

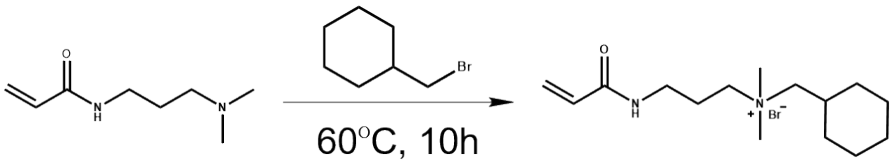

Figure S7. Synthetic route of CDMAPAA.

A mixture of bromomethylcyclohexane (5 g, 28 mmol) and N,N-dimethylpropylacrylamide (5.31 g, 34 mmol) in ultra-dry acetonitrile (20 mL) was stirred at

60°C for 10 h under N_2 atmosphere in a 25 mL Schlenk bottle. After precipitated by ether, the crude product was dissolved and precipitated three times with methanol and ether to remove impurities, and dried under vacuum to obtain the product CDMAPAA as pale-yellow viscous liquid. Yield: 54%. ESI-MS (*m/z*): $[M\text{-}Br]^+$ calcd. for $C_{15}H_{29}N_2O^+$: 253.2274; found: 253.2280. The ^1H NMR spectrum is shown in Figure S8, and the mass spectrum result is shown in Figure S9.

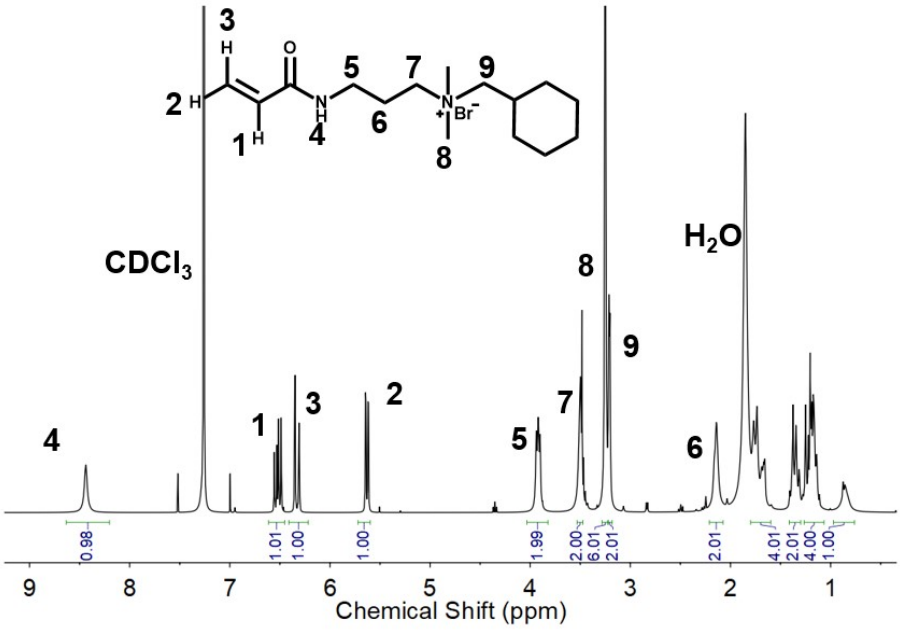

Figure S8. ^1H NMR (400 MHz) spectrum of CDMAPAA in $CDCl_3$.

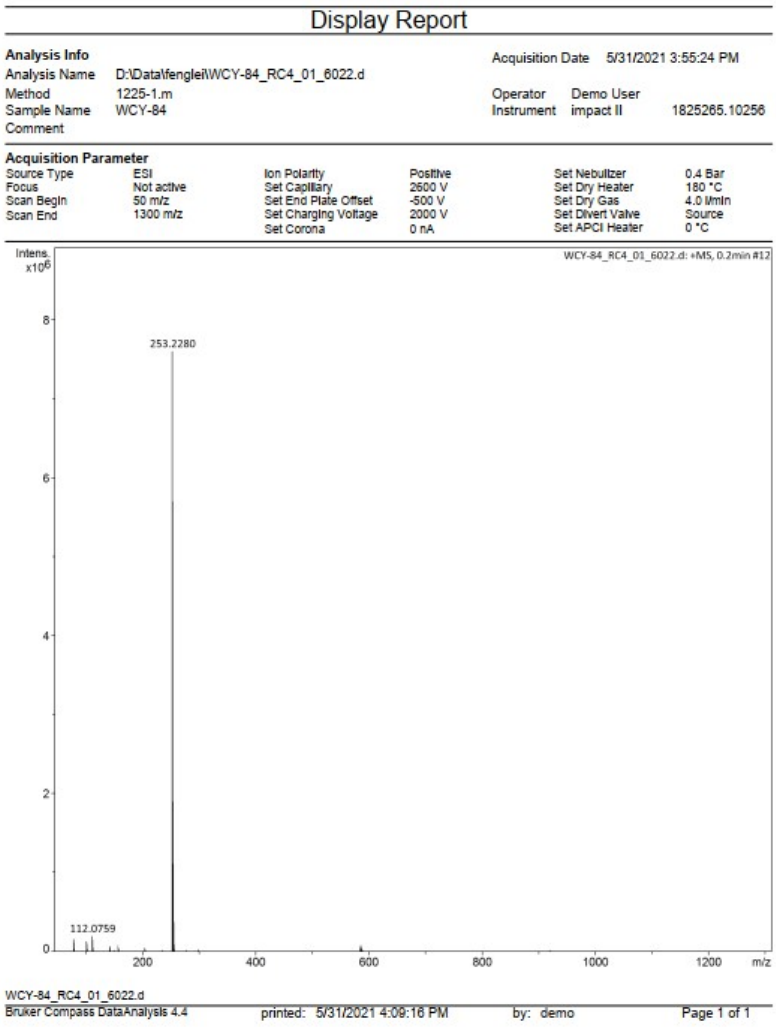

Figure S9. ESI mass spectrum of CDMAPAA.

4. Synthesis of $AA_1CB[7]$

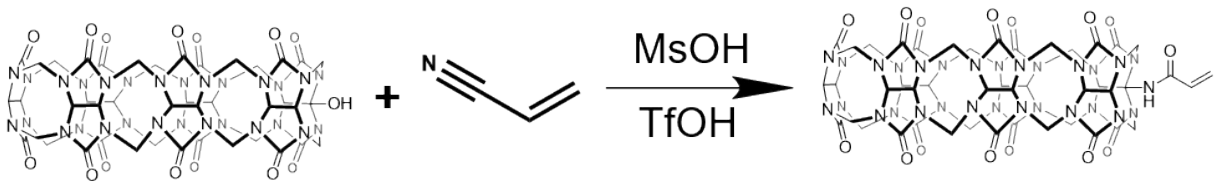

Figure S10. Synthetic route of $AA_1CB[7]$.

The synthesis of monoacrylamide CB[7] ($AA_1CB[7]$) was slightly modified according to the literature method[1]. C8bim·HOCB [7] (1.5 g, 0.9 mmol) and acrylonitrile (1.0 g, 20 mmol)

were dispersed in 20 mL of methanesulfonic acid in ice bath. Ice trifluoromethanesulfonic acid (10 g) was added to the above-mentioned methanesulfonic acid mixed solution and reacted at 50°C for 4 h. The solution was precipitated by excess acetone to obtain a yellow viscous solid. The target product $AA_1CB[7]$ as white powder was obtained after separation and purification by column chromatography. Yield: 85%. The ^1H NMR spectrum is shown in Figure S11.

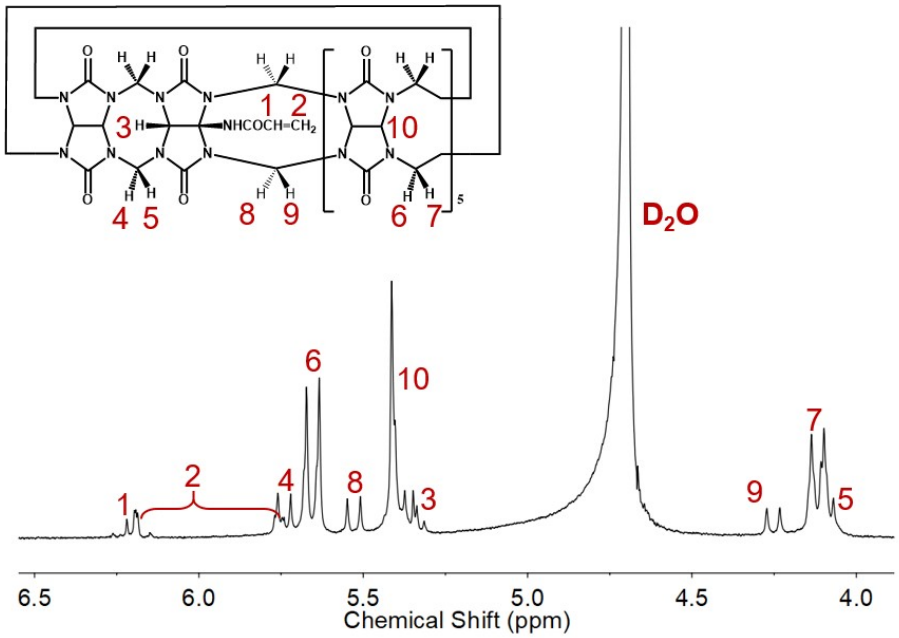

Figure S11. ^1H NMR (400 MHz) spectrum of $AA_1CB[7]$ in D_2O.

5. Components of A_x-HG_y hydrogels

Table S1. Components of A_x-HG_y hydrogels.

Sample	Aam (g)	ADMAPAA/Aam (mol%)	CDMAPAA/Aam (mol%)	AA_1CB[7]/Aam (mol%)
A_0-$HG_{0.10}$	1.0	0	0.10	0.10
$A_{1.0}$-$HG_{0.10}$	1.0	1.0	0.10	0.10
$A_{2.0}$-$HG_{0.10}$	1.0	2.0	0.10	0.10
$A_{3.5}$-$HG_{0.10}$	1.0	3.5	0.10	0.10
$A_{5.0}$-$HG_{0.10}$	1.0	5.0	0.10	0.10
$A_{7.0}$-$HG_{0.10}$	1.0	7.0	0.10	0.10
$A_{2.0}$-HG_0	1.0	2.0	0	0
$A_{2.0}$-$HG_{0.15}$	1.0	2.0	0.15	0.15
$A_{2.0}$-$HG_{0.20}$	1.0	2.0	0.20	0.20
$A_{2.0}$-$HG_{0.35}$	1.0	2.0	0.35	0.35
$A_{2.0}$-$HG_{0.50}$	1.0	2.0	0.50	0.50

The content of APS, TMEDA and H_2O of all these samples are 0.01 g, 17 μL and 5 mL, respectively.

6. Intermolecular interaction

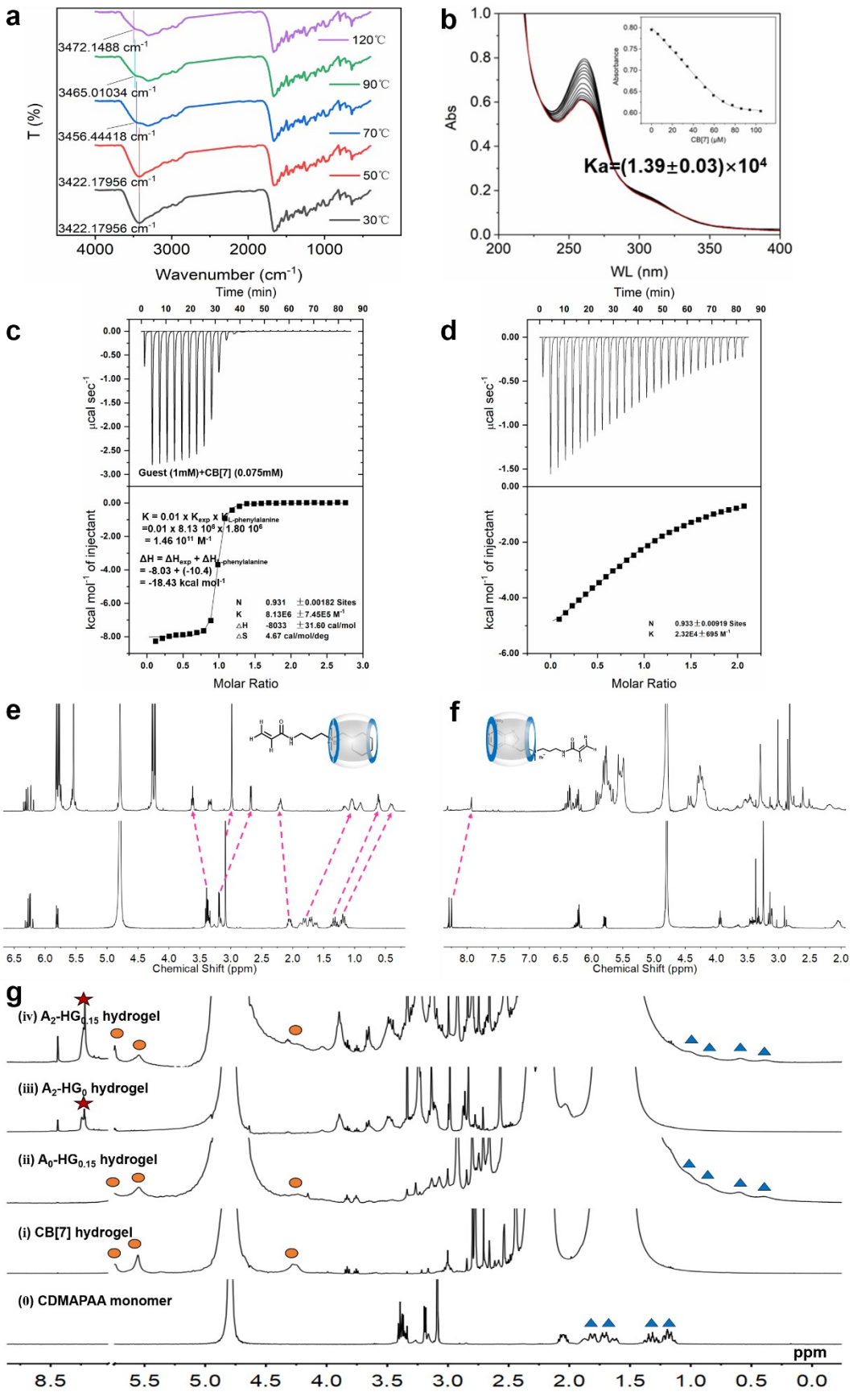

Figure S12. (a) Variable temperature infrared spectra of ADMAPAA. (b) UV-vis spectra of ADMAPAA upon the titration of CB[7]. (c) ITC curves of AA_1CB[7] upon the competitive titration of CDMAPAA and ADA. (d) ITC curves of AA_1CB[7] upon the titration of ADMAPAA. (e) The binding sites of CDMAPAA and AA_1CB[7] in D_2O measured by ^1H NMR spectra. (f) The binding sites of ADMAPAA and AA_1CB[7] in D_2O measured by ^1H NMR spectra. (g) ^1H NMR spectra of (0) CDMAPAA monomer, (i) hydrogel polymerized by acrylamide and AA_1CB[7], (ii) hydrogel cross-linked by AA_1CB[7] and CDMAPAA, (iii) hydrogel cross-linked by ADMAPAA and (iv) ADMAPAA and AA_1CB[7]@CDMAPAA dual-cross-linked hydrogel. The spectra were recorded in D_2O. The peaks of CB[7], cyclohexane unit and adenine unit were indicated with orange dots, blue triangles and red stars, respectively.

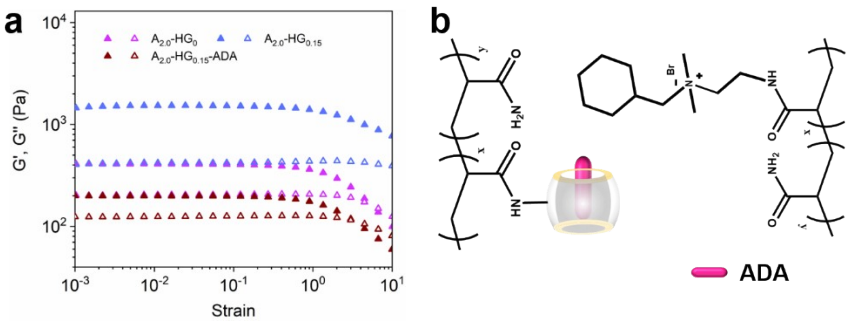

Figure S13. (a) Oscillation amplitude sweeps of hydrogels with or without competitor ADA. (b) Schematic of CDMAPAA and AA_1CB[7] occupied by ADA in the polymer network.

7. Mechanical properties of A_x-HG_y hydrogels

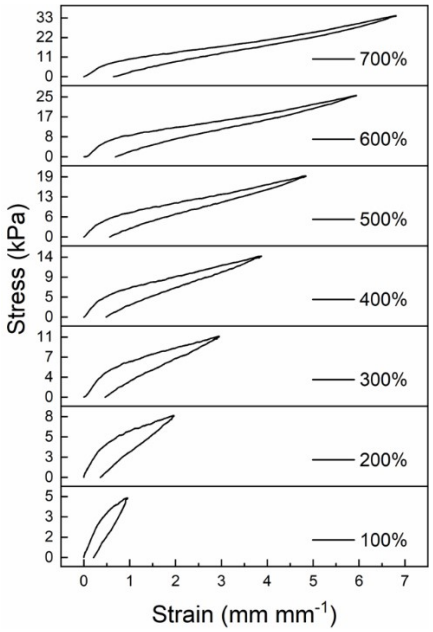

Figure S14. Tensile loading-unloading tests of $A_{2.0}$-$HG_{0.15}$ hydrogel at different setting strains.

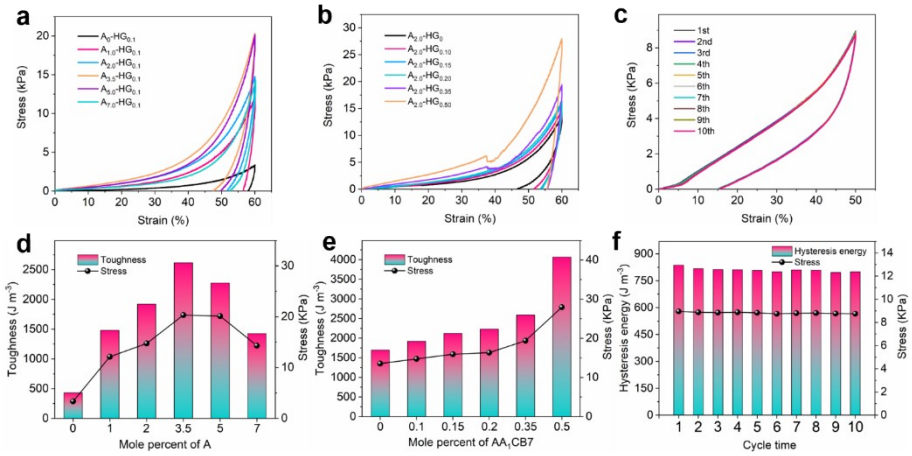

Figure S15. The compress performance of hydrogels with different content of (a) ADMAPAA and (b) $AA_1CB[7]$@CDMAPAA. (c) Continuous 10 compressive cyclic loading-unloading curves of the $A_{2.0}$-$HG_{0.15}$ hydrogel. (d-f) Corresponding stress, toughness and hysteresis energy.

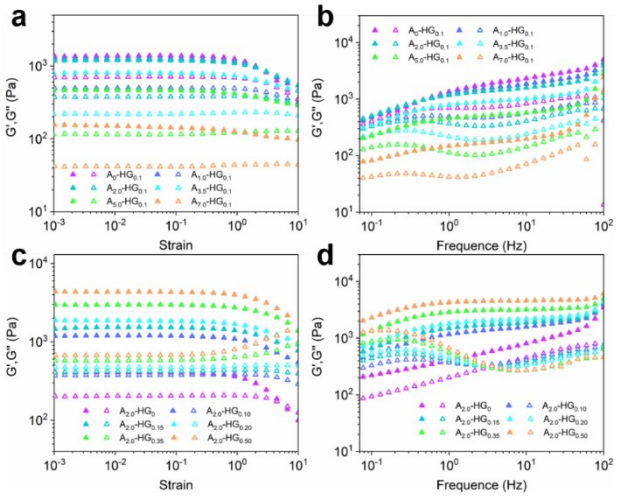

Figure S16. (a) Oscillation amplitude sweeps and (b) frequency sweeps of hydrogels with different content of ADMAPAA. (c) Oscillation amplitude sweeps and (d) frequency sweeps of hydrogels with different content of $AA_1CB[7]$@CDMAPAA. The solid marks represent the storage modulus (G′) and the hollow marks present the loss modulus (G″).

8. Adhesion properties of A_x-HG_y hydrogels

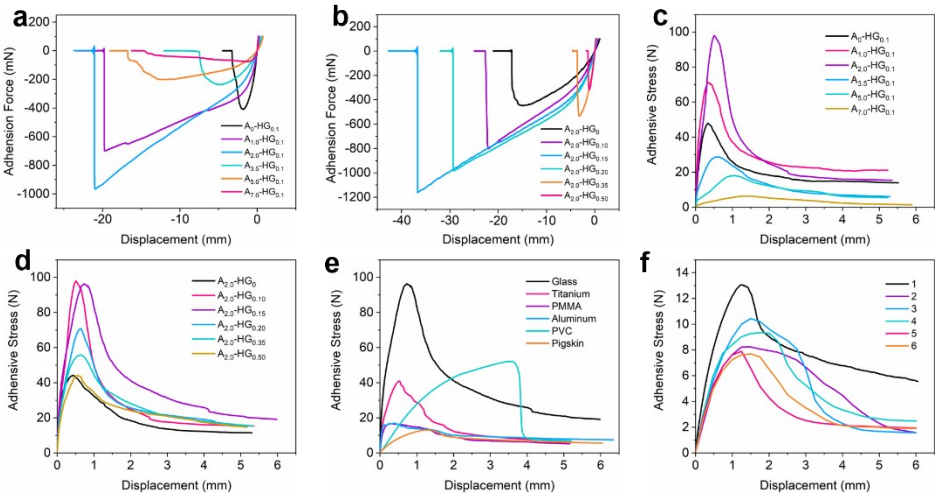

Figure S17. Mechanical contact curves of hydrogels with different content of (a) ADMAPAA and (b) $AA_1CB[7]$@CDMAPAA. Lap shear test curves of hydrogels with different content of

(c) ADMAPAA and (d) AA_1CB[7]@CDMAPAA. (e) Lap shear test curves of $A_{2.0}$-$HG_{0.15}$ hydrogel toward different substrates. (f) Cyclic lap shear test curves of $A_{2.0}$-$HG_{0.15}$ hydrogel toward pigskin.

9. Electrical performance of A_x-HG_y hydrogels

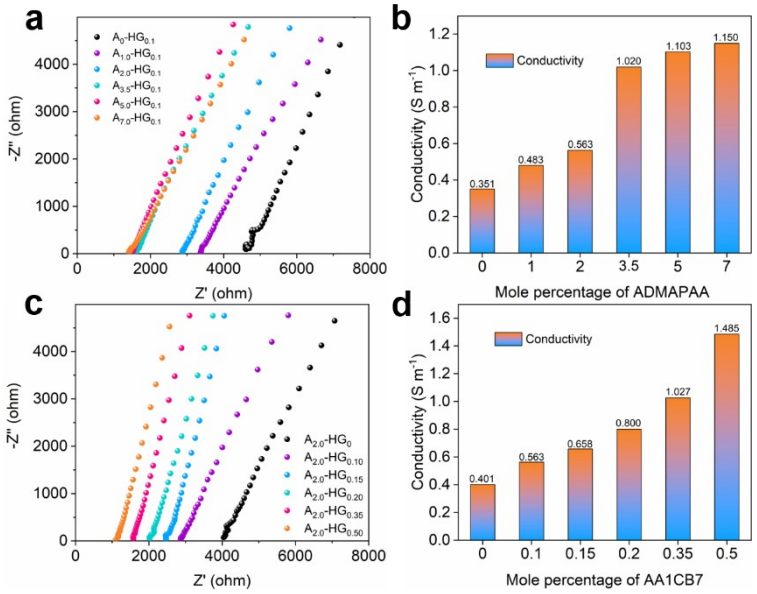

Figure S18. (a) EIS spectra and (b) conductivity of hydrogels with different content of ADMAPAA. (c) EIS spectra and (d) conductivity of hydrogels with different content of AA_1CB[7]@CDMAPAA.

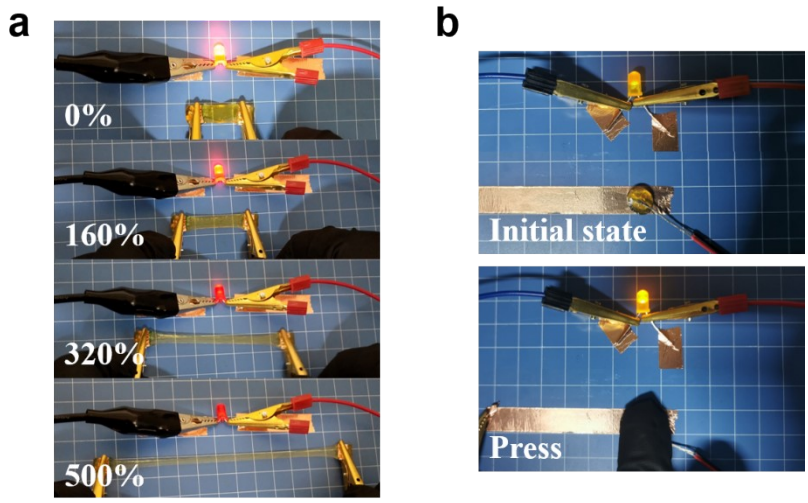

Figure S19. The brightness changes of LED lamp under (a) different tensile strain or (b) compression of $A_{2.0}$-$HG_{0.15}$ hydrogel.

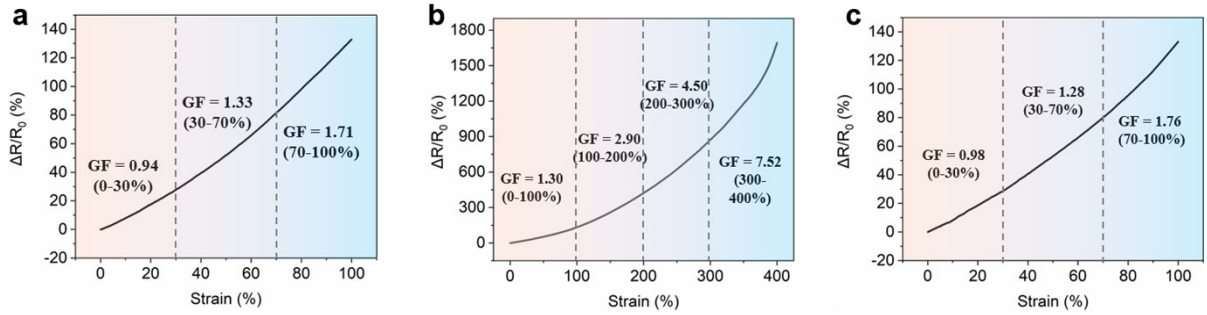

Figure S20. (a) RRV of $A_{2.0}$-$HG_{0.15}$ hydrogel with a segmented strain region of 0-100%. (b, c) RRV of experimental group hydrogel with a segmented strain region.

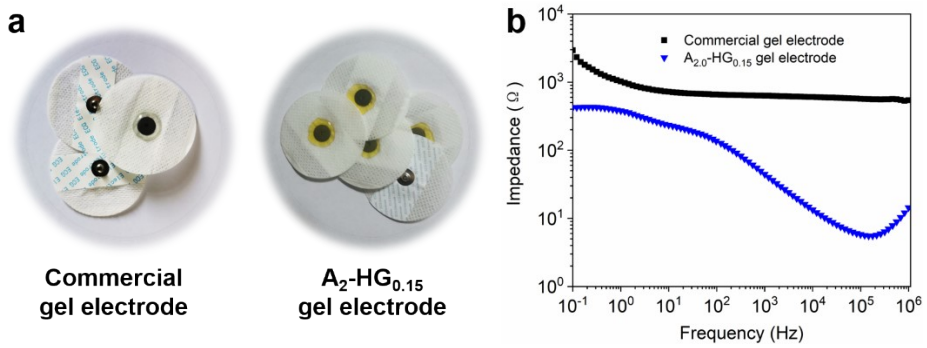

Figure S21. (a) Photos of commercial gel electrode and $A_{2.0}$-$HG_{0.15}$ gel electrode. (b) $A_{2.0}$-$HG_{0.15}$ gel electrode had a lower electrical impedance in different frequency, compared with commercial gel electrode.

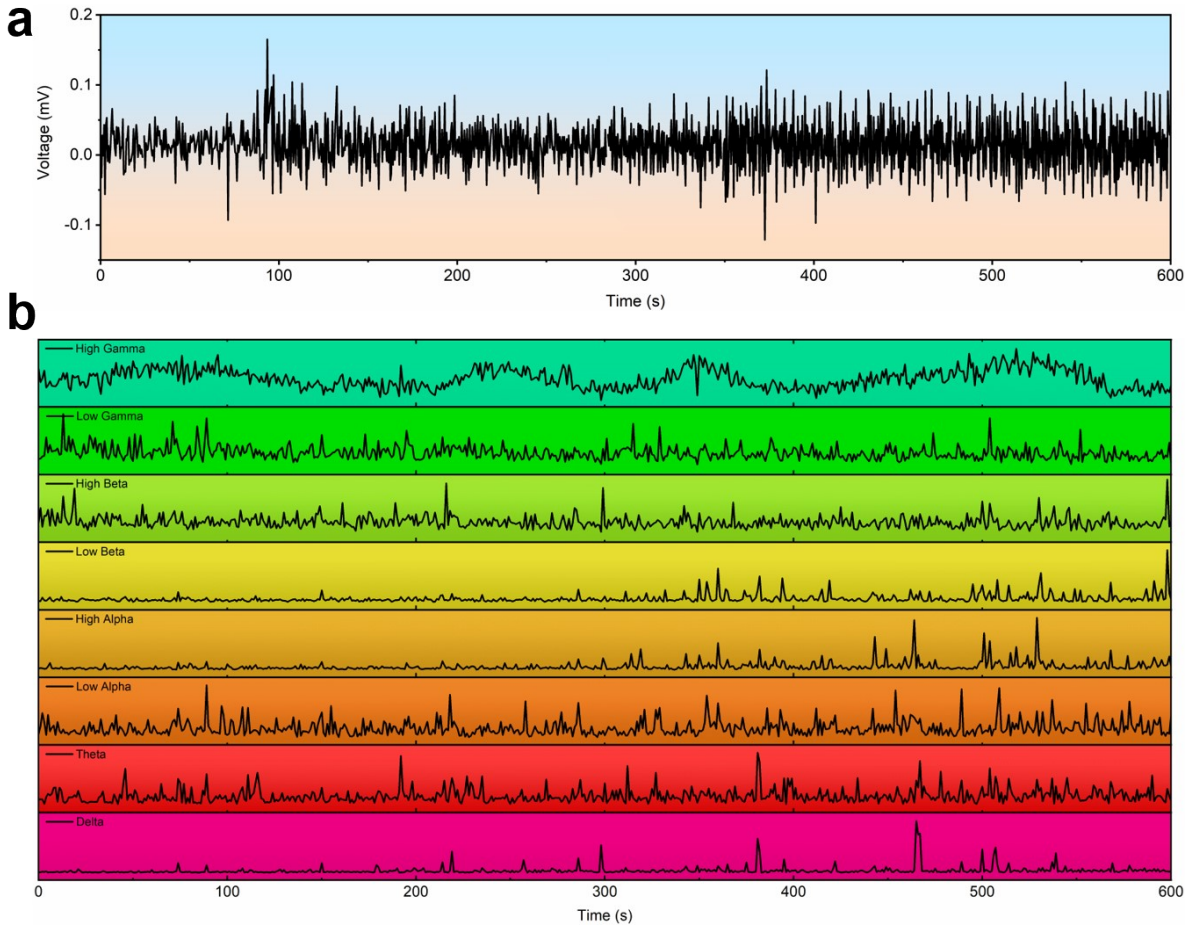

Figure S22. (a) EEG recorded by $A_{2.0}$-$HG_{0.15}$ gel electrode during sleep. (b) EEG (delta, theta, low alpha, high alpha, low beta, high beta, low gamma and high gamma) recorded by $A_{2.0}$-$HG_{0.15}$ gel electrodes during sleep.

Reference

1. S. K. Ghosh, A. Dhamija, Y. H. Ko, J. An, M. Y. Hur, D. R. Boraste, J. Seo, E. Lee, K. M. Park and K. Kim, *Journal of the American Chemical Society*, 2019, **141**, 17503-17506.