

## Supporting information

### Fluorescent, Electric Responsive and Ultratough Self-Healing Hydrogels via Bioinspired All-in-One Hierarchical Micelle

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## Methods

**Materials.** 2-amino-4[1H]-6-methylpyrimidinone, hexamethylene diisocyanate (HDI, 98%), Acrylamide (AM, 99%) and Dibutyltin dilaurate (DBTDL) were purchased from J&K Chemical Ltd. (Beijing, China). 4-Hydroxybutyl acrylate (> 98%) and sodium dodecyl sulfate (SDS, 98%) were purchased from Heowns Biochemical Technology Co., Ltd. (Tianjin, China). 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS, 98%) was purchased from Alfa Aesar. Co. Ltd. (Tianjin, China). All chemicals and solvents were used without any further purification, unless otherwise stated.

**Preparation of UPyHCBA monomer.** 4-(6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido) hexylcarbamoyloxy)-butyl acrylate (UPyHCBA) monomer was synthesized according to the procedure reported in the literature,<sup>1</sup> as also shown in Scheme S1. First of all, 2-(6-Isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidin-one (UPy-HDI) was synthesized using a reported procedure.<sup>2</sup> Then, a mixture of UPy-HDI (1.5 g, 5.1 mmol) and 4-hydroxybutyl acrylate (0.81 g, 5.61 mmol) was reacted in 100 ml of CHCl<sub>3</sub> in the presence of 40  $\mu$ l of DBTDL, and the mixture was allowed to magnetic stirring at room temperature for 24 h. Then, the solvent was removed under reduced pressure and the residue was washed with excess acetone at least 3 times. After being dried in vacuum, 1.8 g of solid white product was obtained ( $\approx$  81% yield), denoted as UPyHCBA. The chemical structure of UPyHCBA was determined by solution <sup>1</sup>H NMR spectroscopy (Fig. S1b).

**Preparation of hydrogels.** The hydrogels were prepared by micellar copolymerization of AM, AMPS with UPyHCBA conducted at 60°C for 10 hours in the presence of KPS. First, NaCl (1.169

g) was dissolved in 40 ml of deionized water at room temperature and then added SDS (3.200 g) to the solution (PH=8.16), and the mixture was stirred at 35°C for half an hour. AMPS (0.25 M) was added to the mixture and stirred for another 1h at 35°C, and then added UPyHCBA(16 mM) stirring for another 2h, yielding a transparent UPyHCBA/SDS-NaCl-AMPS micelles solution. For the micelle copolymerization, AM (4.75 M) and KPS (25 mM) initiator were added and dissolved to the micelle's solution. Finally, the solution was injected into a glass mold and polymerized at 60°C for 10 hours to obtained the hydrogels.

**Characterization.** Solution nuclear magnetic resonance (NMR) experiments were performed on a Bruker AVANCE III NMR spectrometer with a proton resonance frequency of 400.13 MHz. The samples were dissolved in deuterated chloroform, D<sub>2</sub>O or DMSO-d<sub>6</sub> with a small amount of TMS as the internal reference standard. Fourier transform infrared spectroscopy (FTIR) experiments was tested using a Bruker Tensor II spectrometer, equipped with RT-DLaTGS detector, at a scan speed of 1.6 kHz, 16 scans per sample and a resolution of 4 cm<sup>-1</sup>. Hydrogel samples were lyophilized before recording the FTIR spectra. The transmittance of SDS-NaCl-AMPS, SDS-NaCl-AMPS-UPyHCBA or SDS-NaCl-UPyHCBA micelle solutions and ultraviolet spectra of different copolymer solutions were measured by using Ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu UV-Vis 2450). The UV-vis spectra were performed on a JASCO V-570 spectrophotometer. The excitation and emission spectra and quantum yield of samples were tested by FS5 EDINBURGH fluorescence spectrometer. The slits of excitation and emission were 1.2nm with the response time of the instrument 0.1s. The slits of excitation and emission slits were 5nm and 0.5nm, respectively, in the quantum yield test. All the tests were carried out at room temperature. Olympus BX51 fluorescent microscopy was applied to take fluorescent images. The

dynamic light scattering (DLS) experiments were conducted at a scattering angle of  $90^\circ$  at  $37^\circ\text{C}$  using a Zetasizer Nano ZS90 (Malvern Instruments, UK) to determine the micelle size of SDS, SDS-NaCl, SDS-NaCl-AMPS or SDS-NaCl-AMPS-UPyHCBA which were calculated using the Malvern application software. The measurements were repeated thrice for each sample at least.

**Mechanical tests.** All mechanical measurements were performed at room temperature on a UTM6103 mechanical testing instrument (Shenzhen Suns Technology Stock Co., LTD., China) in tensile mode with a stretching speed of  $50\text{ mm min}^{-1}$  for uniaxial tensile measurements and  $100\text{ mm min}^{-1}$  for loading-unloading tests. For uniaxial tensile measurements, rectangular test strips were prepared from the sample using a knife and a thickness of  $0.8\text{--}1.2\text{ mm}$ , measured for each sample with an SFJ digital thickness tester. At least three duplicates were tested for each hydrogel, and the mean value of the mechanical parameters was calculated. The elastic modulus (E) was calculated from the slope of the initial linear region of the stress–strain curve with strain below 10%, while the toughness was measured by the area under the stress–strain curve until sample fracture using integration. For loading-unloading tests, the hydrogels were first stretched to a maximum strain of 500% and then unloaded. The samples were sealed in a plastic bag, stored at room temperature, then removed and stretched again at the prescribed time to evaluate their resilience. The dissipated energies were estimated by the loop area between the loading–unloading profiles. The recovery ratio was defined as the ratio of dissipated energy after a specific waiting time to that in the first loading-unloading test.

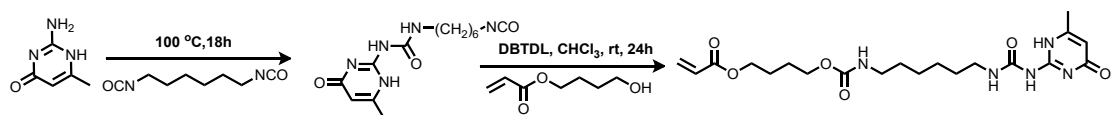
**Measurement of healing behaviour.** A rectangular test strips ( $30\text{ mm} \times 8\text{ mm}$  and thickness of  $0.8\text{ mm}$ ) was cut into two sections. The two freshly cut surfaces of the sample were tightly placed together storing in a sealed plastic bag at room temperature. After 12 h, tensile tests were carried

out at room temperature using the same method mentioned above.

**Rheological measurements.** The rheological behavior of hydrogels were conducted using a rheometer (TA AR2000ex) at 37°C, employing a set of parallel plates with 40 mm diameters. The edge of the sample was coated with silicone oil to prevent desiccation. Oscillatory frequency sweep measurement was conducted at 0.01% strain amplitude. Oscillatory strain amplitude sweep measurement was conducted at 6.28 rad/s frequency. Furthermore, step-strain sweep measurements were conducted to evaluate the self-healing properties of hydrogels on the applied alternate shear force (Fig. S3).

**Electro-Induced bending behavior experiment.** The as-prepared A<sub>4.75</sub>-S<sub>0.25</sub>-U<sub>16</sub> hydrogels were cut into a strip with dimension of 20 mm × 2 mm × 2 mm (length × width × thickness) for using to investigate the electro-induced bending behaviors. The methyl orange was used to dye the samples for easy observation. The electric field actuation device was described in Fig. 5a. Two graphite electrodes in Na<sub>2</sub>SO<sub>4</sub> solution (0.01 M, 0.05 M, 0.1 M or 0.15 M) were parallelly placed with a distance of 85 mm, which were connected to a DC power with certain supply voltage (15 V, 20V, 25 V or 30 V). Besides, the hydrogel strip, with one end fixed with a clamp, was put in the center of the electric field actuation device. With everything in place, the DC power could be turn on, while the hydrogel bent immediately, and the bending angle of the hydrogel strip deformation was recorded by a digital camera every 20 seconds, which is defined as the degree that hydrogels deviate from the original location (the bending angle of the hydrogels at the initial position is defined as 0°). At least three duplicates were tested for each parallel test, and the mean value of the bending angle was calculated.

## Supplementary Scheme



**Scheme S1** Synthetic procedures of UPyHCBA

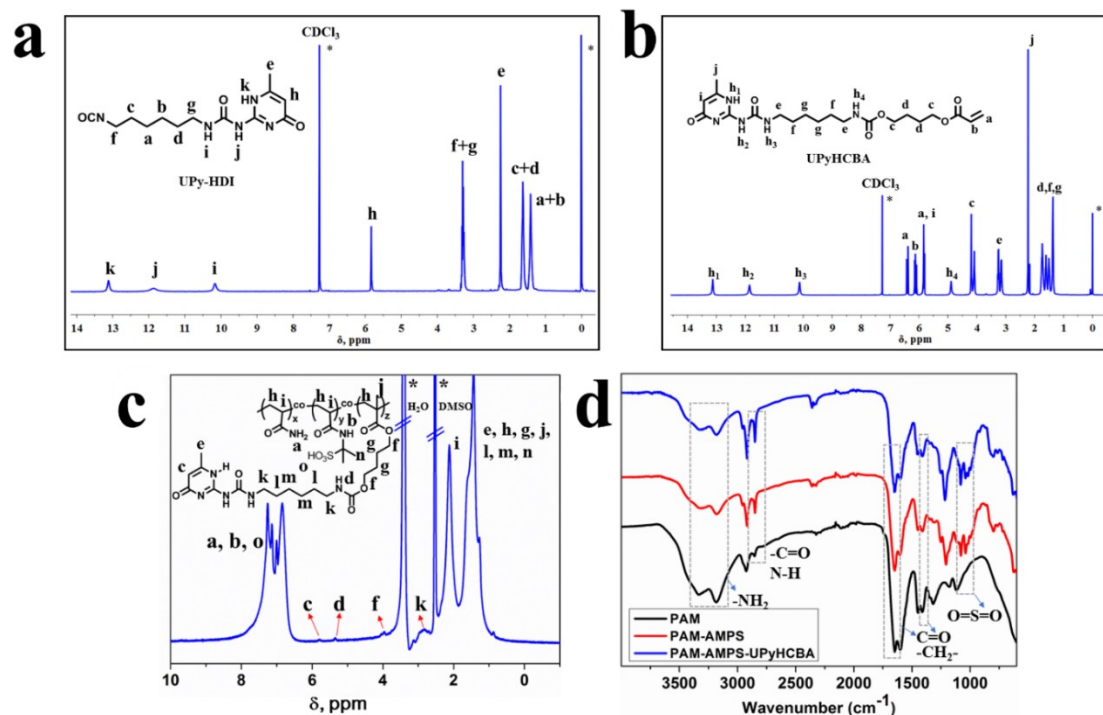
## Supplementary Table

**Table S1** Recipes and mechanical properties of hydrogels

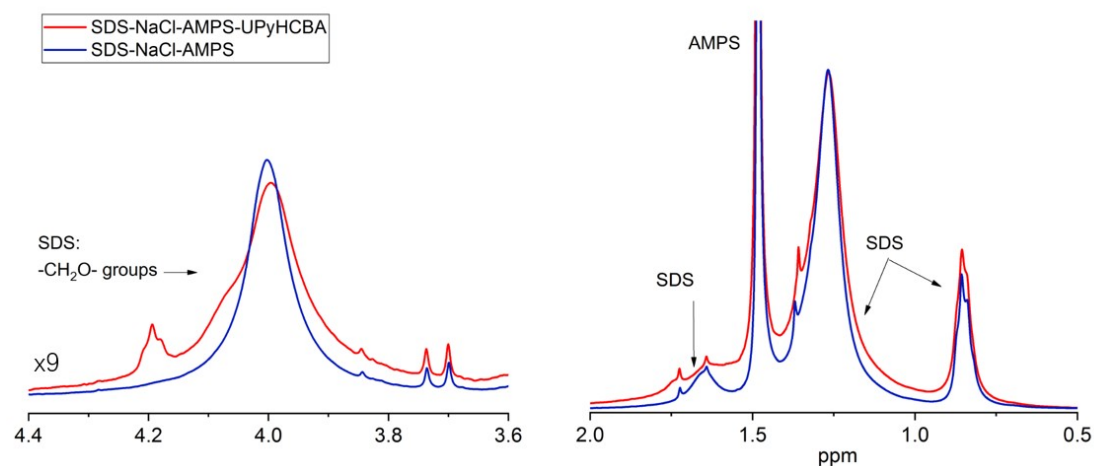
Samples	AM (mol/L)	AMPS (mol/L)	UPyHCBA (mmol/L)	$\sigma_b$ (kPa)	$\varepsilon_b$ (%)	$E_b$ (kPa)	$W_b$ (kJ / m <sup>3</sup> )
A <sub>4.75</sub> -S <sub>0.25</sub> -U <sub>0</sub>	4.75	0.25	0	66	787	4.7	303
A <sub>4.75</sub> -S <sub>0.25</sub> -U <sub>6.8</sub>	4.75	0.25	6.8	83.4	1023	5.6	511
A <sub>4.75</sub> -S <sub>0.25</sub> -U <sub>11.4</sub>	4.75	0.25	11.4	103	1179	9.1	724
A <sub>4.75</sub> -S <sub>0.25</sub> -U <sub>16</sub>	4.75	0.25	16	185	1511	11.8	1470
A <sub>4.75</sub> -S <sub>0.25</sub> -U <sub>22.8</sub>	4.75	0.25	22.8	214	1311	17	1479
A <sub>4.85</sub> -S <sub>0.15</sub> -U <sub>16</sub>	4.85	0.15	16	79.1	1201	4.2	519
A <sub>4.8</sub> -S <sub>0.2</sub> -U <sub>16</sub>	4.8	0.2	16	82.7	1413	6	596
A <sub>4.7</sub> -S <sub>0.3</sub> -U <sub>16</sub>	4.7	0.3	16	238	1518	16.4	1678

$\sigma_b$ ,  $\varepsilon_b$ ,  $W_b$ , and  $E_b$  are the tensile stress, fracture strain, toughness, and elastic modulus, respectively.

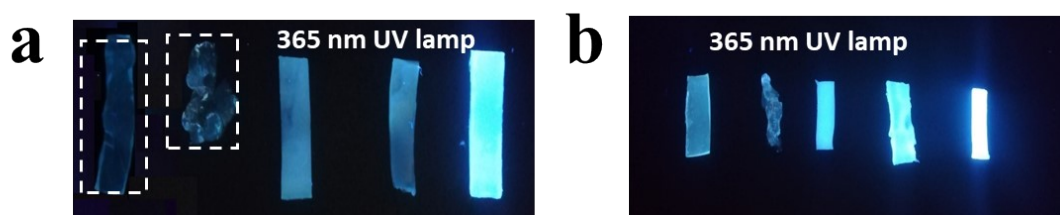
## Supplementary Figures



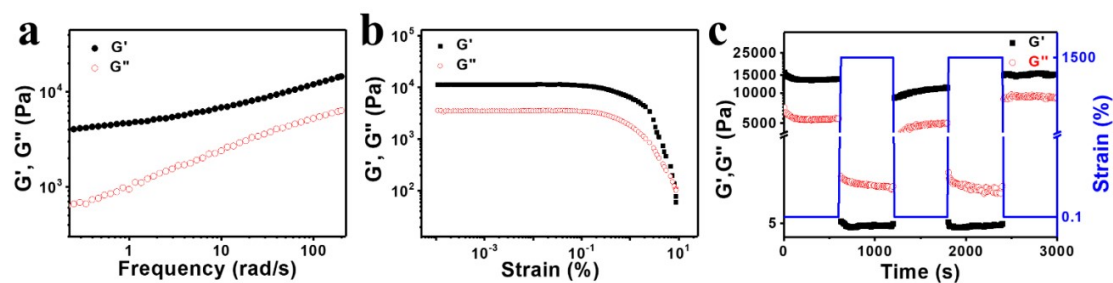
**Fig. S1**  $^1\text{H}$  NMR spectrum of UPy-HDI (a) and UPyHCBA (b) in  $\text{CDCl}_3$ . “\*” indicates the proton signals of chloroform ( $\delta_{\text{iso}} = 7.26$  ppm) and TMS ( $\square \delta_{\text{iso}} = 0$  ppm). (c)  $^1\text{H}$  NMR spectra of PAM-AMPS-UPyHCBA copolymer in  $\text{DMSO-d}_6$ . (d) FTIR spectra of dry PAM-AMPS-UPyHCBA hydrogels. Key assignments were indicated by the dash rectangle in the figure.



**Fig. S2**  $^1\text{H}$  NMR spectrum of SDS-NaCl-AMPS (blue) and SDS-NaCl-AMPS-UPyHCBA (red) micelles in  $\text{D}_2\text{O}$ . The spectrum of  $-\text{CH}_2\text{O}-$  groups of SDS from 4.4 to 3.6 ppm was magnified by 9 times.



**Fig. S3** Photos of (a) hydrogel under 365 nm UV lamp (from left to right: PAMPS, P(AM-AMPS), SDS/PAM, SDS/P(AM-AMPS), SDS/P(AM-AMPS-UPyHCBA)), (b) corresponding dry gel under 365 nm UV lamp.



**Fig. S4** Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of the hydrogel at different frequencies with fixed strain amplitude (0.01%) (a), in a strain range of 0.1-10 with fixed frequency (6.28 rad/s) (b). (c) Time sweep rheological test of hydrogel when alternated step strain was applied (The small strain was 0.1%, and the large strain was 1500%).



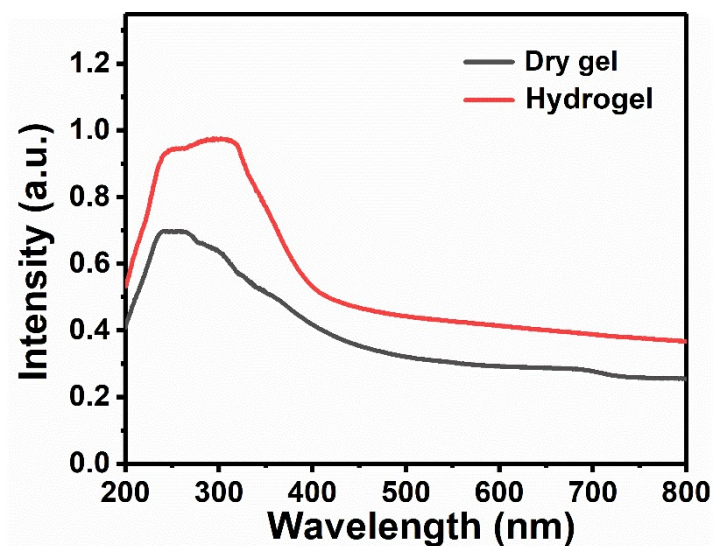


Fig. S5 UV-vis spectra of dry gel and hydrogel.

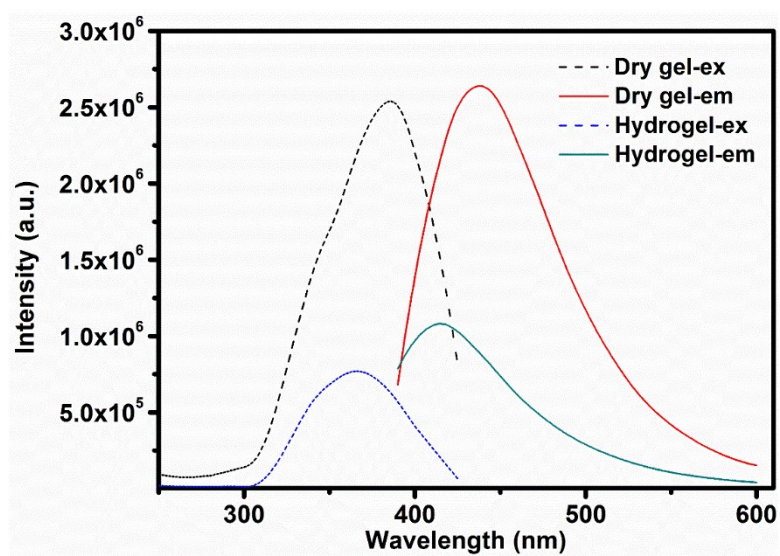


Fig. S6 Excitation (left, dotted line) and emission (right, solid line) spectra of  $A_{4.75}\text{-}S_{0.25}\text{-}U_{16}$  hydrogel and dry gel (Excitation and emission wavelength are 365 and 445 nm for hydrogel, 380 and 435 nm for dry gel, respectively).

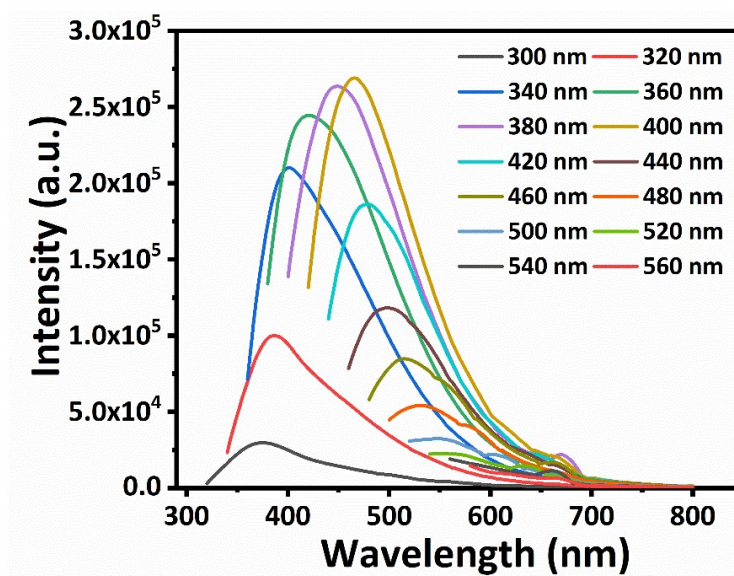


Fig. S7 Excitation-dependent photoluminescence of gel at varying excitation wavelengths.

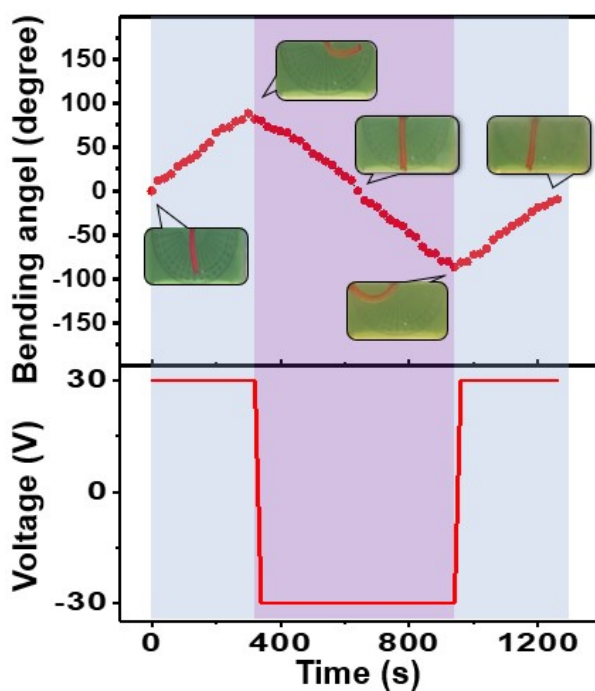
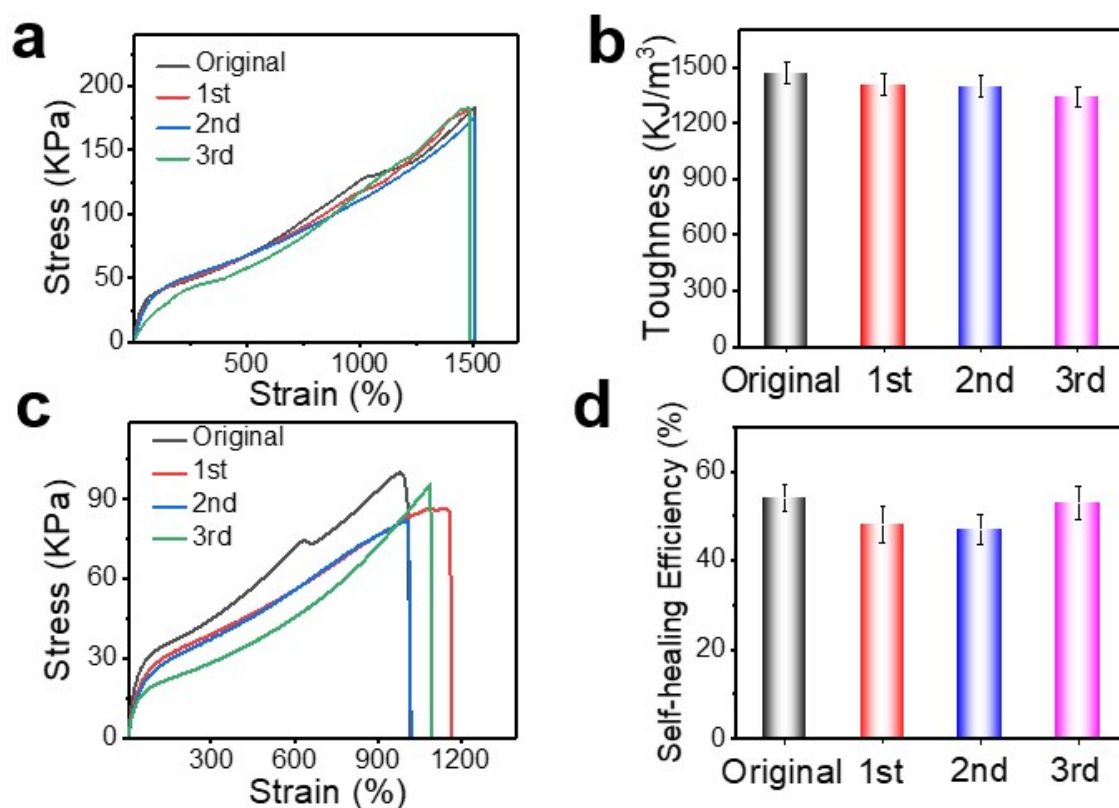


Fig. S8. The reversible bending behavior of  $A_{4.75}\text{-}S_{0.25}\text{-}U_{16}$  hydrogel in 0.05 M  $\text{Na}_2\text{SO}_4$  aqueous solution with the periodical changing electric field of 30 V and -30 V.



**Fig. S9.** (a) Tensile stress-strain curves of the  $A_{4.75}\text{-}S_{0.25}\text{-}U_{16}$  hydrogels after tolerating different times stimuli of the electric pulse, and the corresponding toughness of the hydrogels (b). (c) Tensile stress-strain curves of the self-healing  $A_{4.75}\text{-}S_{0.25}\text{-}U_{16}$  hydrogels, and the corresponding self-healing efficiency of the hydrogels (d). The 1st-3rd tests were performed on the gels with 5 min, 10 min and 15 min of exposure to electric stimuli, respectively.



**Fig. S10.** Photographs of  $A_{4.75}\text{-}S_{0.25}\text{-}U_{16}$  hydrogels under a 365 nm UV lamp (from left to right: original sample, the 1st-3rd test were performed on the gels with 5 min, 10 min and 15 min of exposure to electric stimuli).

### Supplementary Movie

The electro-responsive bending behaviors of hydrogel for lifting the cargo with weight of 0.5 g.

### **Supplementary references**

- S1. I. Jeon, J. Cui, W. R. Illeperuma, J. Aizenberg and J. J. Vlassak, *Adv. Mater.*, 2016, **28**, 4678-4683.
- S2. S. L. Bobade, T. Malmgren and D. Baskaran, *Polym. Chem.*, 2014, **5**, 910-920.