

## Electronic Supplementary Information

### Thermal- and pH-responsive triple-shape memory hydrogel based on a single reversible switch

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#### Materials.

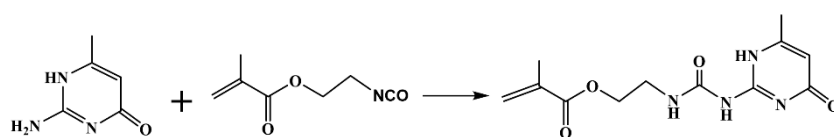
6-methylisocytosine (MIS, 99%, J&K Chemical), 2-Isocyanatoethyl methacrylate (98%, J&K Chemical), 4-(11-hydroxy undecyl oxy)benzaldehyde (98%, TCI), p-hydroxybenzaldehyde (98%, TCI), pyrrole (99%, Macklin), acryloyl chloride (95%, TCI), N, N-dimethylacrylamide (DMAA, 99%, TCI), N, N'-methylene bisacrylamide (MBA, 98%, TCI), ammonium persulphate (APS, 99%, Sinopharm), concentrated hydrochloric acid (HCl, 36~38%, Sinopharm) and calcium hydride (97%, Sinopharm) were used as received.

#### Characterizations

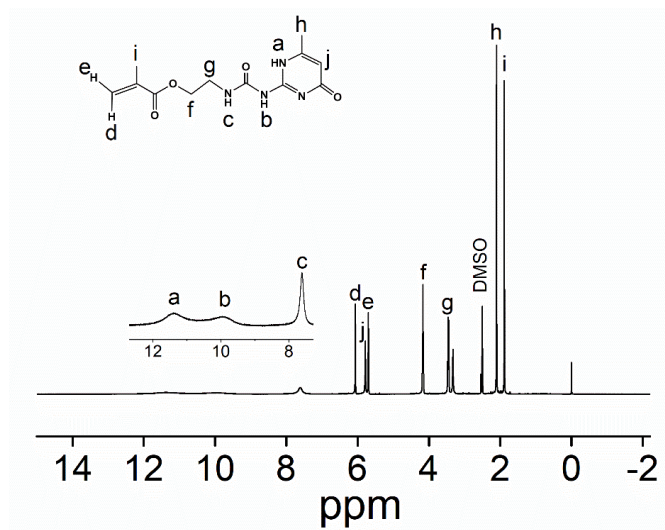
<sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz NMR spectrometer (Bruker BioSpin Co., Switzerland) in DMSO-d<sub>6</sub>. Fracture surface of the dried hydrogel sample was detected with a Hitachi S-4800 scanning electron microscope under 10 kV acceleration voltage after gold sputtering. FTIR examinations were conducted on a Nicolet™ iS50 FTIR spectrometer. Rheological measurements

were performed on a Discovery DHR-3 rheometer (TA Instruments, USA) with a plate-plate geometry (diameter =8 mm). The thermal behavior was characterized by performing temperature ramps at a heating rate of 5 °C min<sup>-1</sup> from 25 to 90 °C at constant angular frequency (10 rad s<sup>-1</sup>). Frequency sweep from 0.1 to 100 rad s<sup>-1</sup> was acquired at 0.1 % strain.

### Synthesis and characterization of 2- (3- (6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl) ureido) ethyl methacrylate (UPyMA)



First, 6-Methylisocytosine (MIS, 2.0 g, 16.0 mmol) was added to 50mL of DMSO dried over calcium hydride and heated up to 170 °C for 10 min. Once the solid dissolved, the oil bath was removed. Then, 2-Isocyanatoethyl methacrylate (2.5 g, 16.1 mmol) was added immediately to the flask under vigorous stirring. The mixture was quickly cooled using an ice water bath. A fine white solid precipitated upon cooling. The precipitate was collected and washed with excess acetone and dried under vacuum. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ<sub>ppm</sub>): 1.89 (s, 3H, CH<sub>3</sub>), 2.11 (s, 3H, ArCH<sub>3</sub>), 3.33-3.50 (m, 2H, NHCH<sub>2</sub>), 4.16-4.21 (t, 2H, OCH<sub>2</sub>), 5.70-5.72 (m, 1H, C=CH<sub>2</sub>), 5.78 (s, 1H, aromatic ring), 6.08(s, 1H, C=CH<sub>2</sub>), 7.63 (s, 1H, NH), 9.86 (s, 1H, NH), 11.42 (s, 1H, NH).



<sup>1</sup>H NMR spectrum of UPyMA in DMSO-d6

### Preparation of hydrogels

The recipes for preparing the hydrogels are listed in Table S1. Different weight ratios of DMAA, UPyMA, MBA and APS were dissolved in DMSO. The mixture was heated up to 85 °C in a sealed tube for 3h, leading to a hydrogel. The resulting hydrogel was first immersed in 2M hydrochloric solution to sufficiently remove DMSO and unreacted monomers, then transferred to deionized water to remove H<sup>+</sup>, and then in a large excess of water for 1 week to remove H<sup>+</sup> and achieve swelling equilibrium. The SEM analysis reveals the hydrogel microstructures. As shown in Fig. S1, the samples with UPy units exhibit a dense structure, indicating a successful formation of quadruple H-bonded crosslinked networks in these hydrogels.

**Table S1. The compositions of the pre-polymerization solution**

Hydrogel sample	UPyMA <sup>a</sup> (wt %)	DMAA <sup>a</sup> (wt %)	MBA <sup>b</sup> (wt %)	APS <sup>b</sup> (wt %)
U0M6	0	100	6	3
U50M6	50	50	6	3
U60M6	60	40	6	3
U70M6	70	30	6	3

<sup>a</sup> UPyMA (wt %) + DMAA (wt %) = 100 (wt %)

$$\frac{MBA/APS}{UPyMA + DMAA} * 100\%$$

<sup>b</sup> MBA/ APS (wt %) =  $\frac{MBA/APS}{UPyMA + DMAA} * 100\%$

The chemical structures of all monomers:

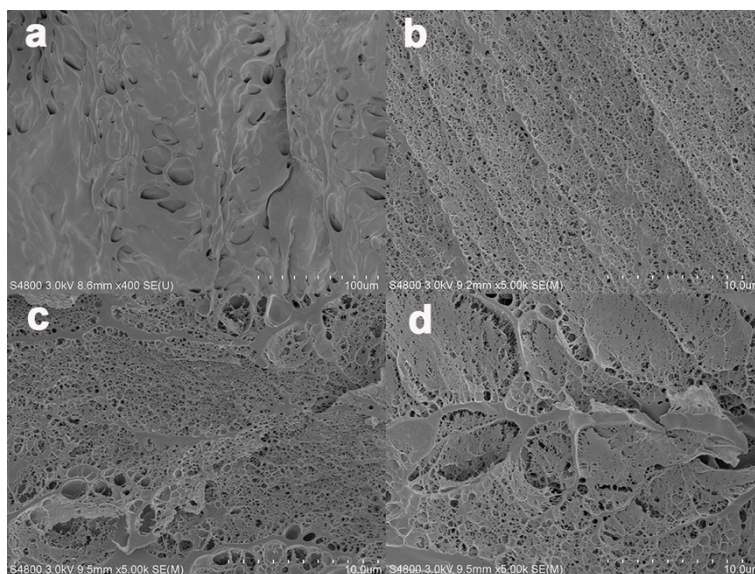
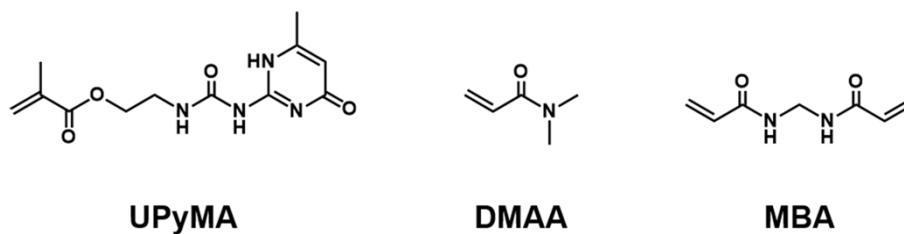
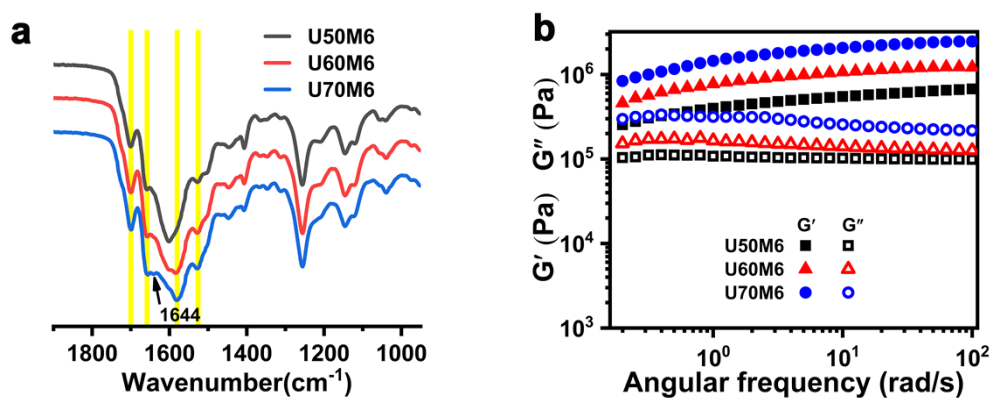


Fig. S1. SEM images of hydrogels with different UPyMA additions: (a) 0 wt%; (b) 50 wt%; (c) 60 wt%; (d) 70 wt%.



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g. S2. (a) FT-IR spectra and (b) dynamic rheological behavior of hydrogels with different content of UPyMA.

We utilized variable-temperature infrared to investigate the dissociation of hydrogen bonds (U70M6) at varying temperatures (80 °C, 85 °C, 90 °C). The obtained results,

depicted in the Fig. S3, demonstrate a gradual decrease in the absorption peaks at  $\sim 1580$   $\text{cm}^{-1}$  of UPy's amide II band with the increase of temperature, indicating a significant temperature-dependent dissociation of hydrogen bonds. This observation underscores the sensitivity of H-bonding to temperature.

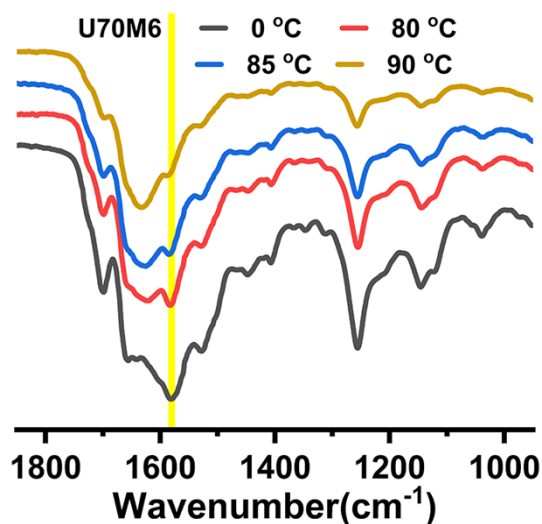


Fig. S3. The FTIR spectra of U70M6 at various temperatures.

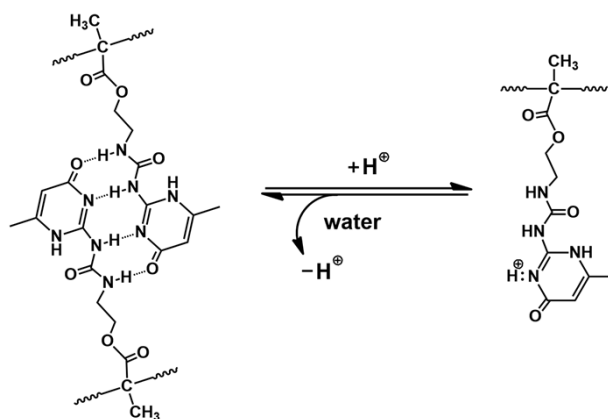


Fig. S4. Protonation/deprotonation equilibria for UPy groups.

### Determination of equilibrium water contents (EWCs) and gel fraction (GF)

The EWCs and GF of the hydrogels were measured at room temperature using a gravimetric method. For EWCs, the hydrogel samples were fully swollen in deionized water. The swollen sample was withdrawn from water and weighed after wiping the surface with an absorbent paper. Afterward, the hydrogels were dried in a vacuum oven

until a constant weight was obtained. The EWCs was calculated according to the following equation:  $EWCs (\%) = (W_s - W_d) * 100 / W_s$ ; where  $W_s$  is the weight of the swollen sample and  $W_d$  is the weight of the dried hydrogel sample. And for GF, the prepared hydrogel samples were dried in a vacuum oven until a constant weight ( $W_1$ ) was obtained. Then, they were weighed again ( $W_2$ ) after fully immersed in DMSO. The gel fraction (GF) was calculated according to:  $GF (\%) = W_2 * 100 / W_1$ .

Table S2. The equilibrium water content (wt%) and gel fraction (wt%) of different hydrogel.

Hydrogel sample	EWCs(%)	GF(%)
U0M6	95.0±1.0	97.0±1
U50M6	81.8±1.5	90.6±1
U60M6	82.5±0.5	91.8±1
U70M6	82.0±0.9	90.9±1

### **Bending test for the determination of the shape memory effect**

The shape memory properties were quantified by applying stress on a rectangular bar by a widely accepted bending test (fold-deploy test) for hydrogels. First, a straight specimen is bent to an angle ( $\theta_0$ ) in 3M HCl solution. The deformed sample was transferred to an aqueous solution for 24 hours to remove  $H^+$  with an external force to maintain the deformation and then a fixing angle ( $\theta_1$ ) is obtained after the deforming stress is released. Second, the sample is immersed in 3M HCl solution and the recovery angle is recorded ( $\theta_2$ ). The fixing ratio ( $R_f$ ) and the recovery ratio ( $R_r$ ) is calculated according to the following equations:  $R_f (\%) = \theta_1 / \theta_0 * 100$ ;  $R_r (\%) = (\theta_1 - \theta_2) / \theta_1 * 100$ .

### **Thermally triggered shape memory effect**

The original shape of the sample (U70M6) is rod-like. After heating to 90 °C, the gel became soft and could easily be bent to a spiral-form shape. This temporary shape was fixed by cooling the sample to 25 °C. It reverted to its original shape within 45s after

immersing the sample in a water bath at 90 °C. The shape memory effect of the system as a consequence of the presence of dynamic UPy units is depicted in Fig. S5. The UPy-based hydrogel fixes the deformation by the dissociation and reassociation of UPy dimers. When the temperature is elevated above the dissociation temperature of the quadruple hydrogen bonding, the covalently cross-linked network structure restores its random coil conformation and the hydrogel reverts to its permanent shape.

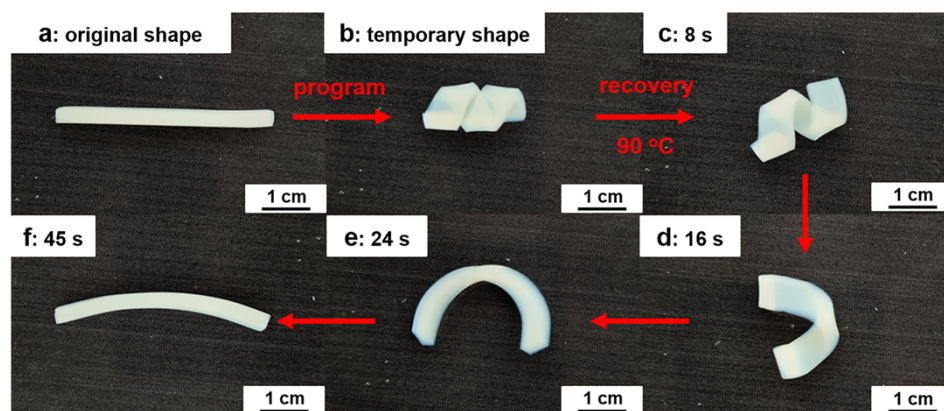


Fig. S5. Shape memory behavior of the hydrogel. (a) A straight specimen was deformed into a spiral-form temporary shape (b) and dropped into a water bath at 90 °C to observe the shape recovery process (c-f), and all processes were recorded by using a digital camera over time.

We assess the shape memory effect upon heat stimulation. The influence of temperature on the fixing ratio and recovery ratio of samples with UPyMA was investigated by performing the shape-fixing process at a certain temperature and then the shape-recovery process at the same temperature. As shown in Fig. S6, all hydrogels exhibit a high shape recovery ratio but show a large difference in shape fixing ratio. We found that the fixation ratio enhanced with increasing temperature, indicating that these UPy dimers serve as phase-transition domains that play a central role in storing the elasticity of the material and fixing the temporary shape. As mentioned in the manuscript, UPy dimers are sensitive to temperature. Therefore, UPy dimers disassociate more completely at higher temperatures, which induces more physical cross-linking points that can be utilized at room temperature to fix the deformation.

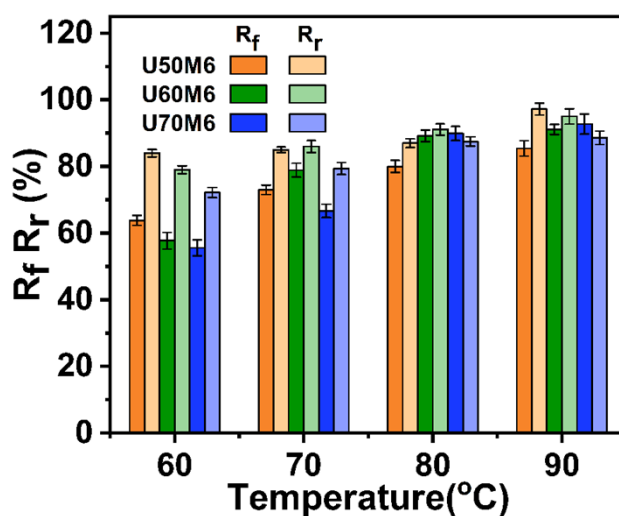


Fig. S6. Effect of temperature on the fixing ratio and recovery ratio of hydrogels with different contents of UPyMA.

### pH triggered shape memory effect

Fig. S7 shows the overall process of shape memory upon pH stimulation. The rod-like sample (U70M6) was bent into a U-shape with external stress after being immersed in 3M HCl solution for 10 min, then transferred to an aqueous solution for 24 hours to fix the temporary shape. It reverted to its original shape within 90s after immersing the sample in 3M HCl solution. Then the sample was transferred to deionized water for 24 h to enable the protonated UPy units are deprotonated and formed UPy dimer again.

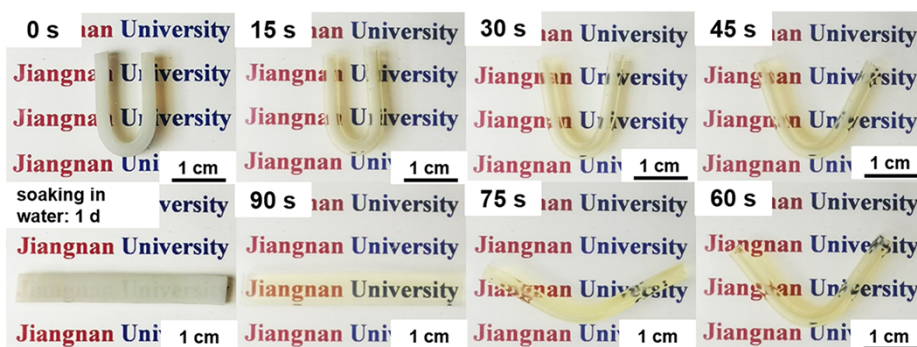


Fig. S7. Photos showing shape memory effect for U70M6 upon pH stimulation.

We carried out a bending test to quantitatively assess the shape memory effect under the trigger of acidic pH. As shown in Fig. S8, all simple with UPy motifs exhibited near-ideal pH-triggered shape memory effect. The  $R_f$  and  $R_r$  of all samples were close



to 100% due to the full dissociation of the H-bond.

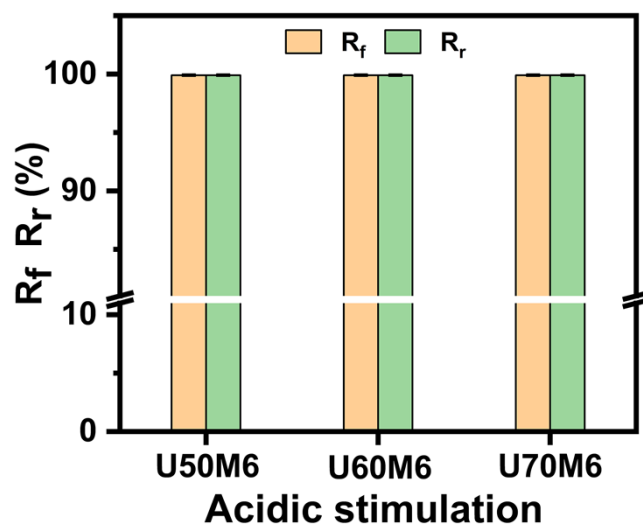


Fig. S8. The shape fixing ratio ( $R_f$ ) and the shape recovery ratio ( $R_r$ ) for hydrogels with various contents of UPyMA upon pH stimulation

### Triple shape memory effect triggered sequentially by temperature and pH.

We attempt to alter the programming sequence of U70M6 in order to investigate the shape memory characteristics. Fig. S9 illustrates the triple-shape memory phenomenon of U70M6, which is activated in a sequential manner by changes in pH and temperature. The initial shape of the sample is a rod (S0). Upon heating to 90 °C, the gel was bent into a spiral-form shape and transferred to a plastic tube to maintain the programmed shape. Subsequently, the sample was immersed in a 0.3M HCl solution (25 °C) for 24 hours to fix the temporary shape (S1). Due to UPy dimers in the hydrogel being in a state of partial dissociation, the sample continued to be programmed into a concave shape (S2). Subsequently, the sample was immersed in an aqueous solution for 24 hours to eliminate H<sup>+</sup>. The temporary shape was fixed with the formation of a hydrogen bonds network. Upon immersion in a 0.3M HCl solution, the sample reverted to a spiral-form shape (S1) within 53 minutes. Furthermore, the sample regained its permanent shape within 45 seconds after being immersed in a water bath at 90 °C.

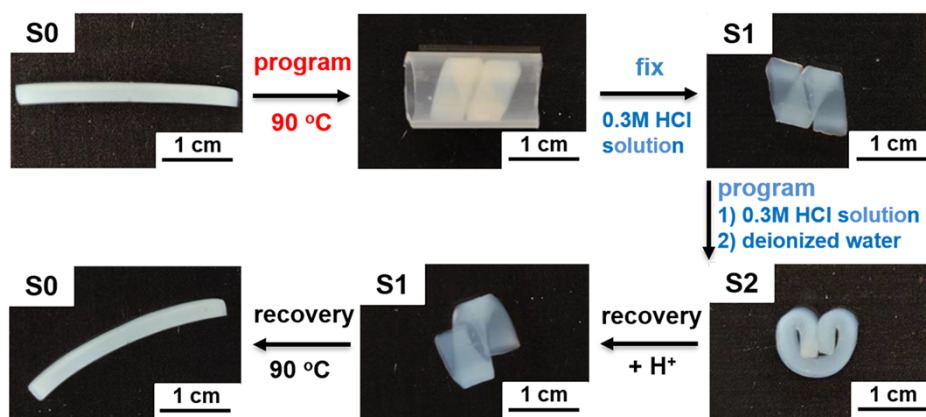


Fig. S9. Photographs of the triple shape memory effect of U70M6 triggered sequentially by pH and temperature.

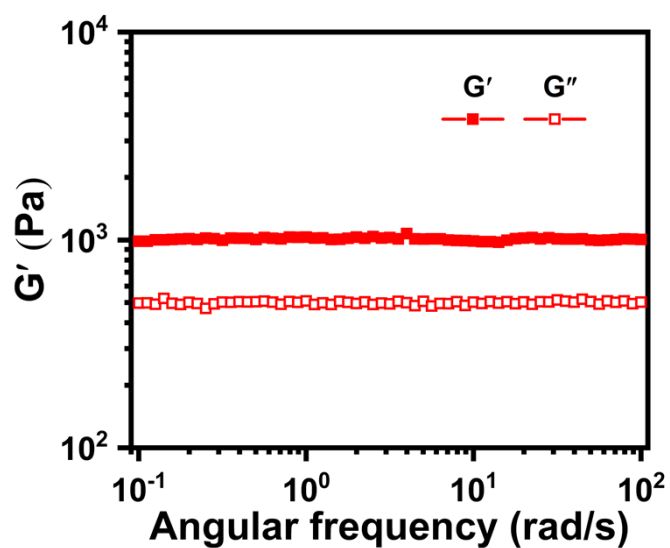


Fig. S10. The storage modulus  $G'$  and loss modulus  $G''$  for hydrogel U0M6.

## REFERENCES

1. K. E. Feldman, M. J. Kade, E. Meijer, C. J. Hawker and E. J. Kramer, *Macromolecules*, 2009, **42**, 9072-9081.