Electronic Supplementary Information (ESI)

pH-switchable and Self-healable Hydrogels based on Ketone type Acylhydrazone Dynamic Covalent Bonds

Zanru Guo,[a]* Wei Ma,[a] Hongjian Gu,[a] Yujun Feng,[b]* Zhanfeng He,[c] Qiang Chen,[a] Xi Mao,[a] Jiali Zhang[a] and Longzhen Zheng[a]

[a]Department of Polymer Materials and Chemical Engineering, School of Materials Science and Engineering, East China Jiao Tong University, Nanchang, Jiangxi 330013, P. R. China

[b]Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, P. R. China.

[c]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation Southwest Petroleum University, Chengdu 610500, P. R. China

Corresponding author. Tel.: +86 0791 87046336; fax: +86 0791 87046320.

E-mail addresses: guozanru@ecjtu.edu.cn (Z. Guo), yjfeng@scu.edu.cn (Y. Feng)

Characterizations

Fig. S1 is the ^{1}H NMR spectra of P_5, P_{10}, P_{20} and P_{30} in D_2O. The signals at 0.7-1.7 ppm is the protons of CH_2 in main chains and $(CH_3)_2C$ in DAAM side chain). The signals at 1.7-2.4 ppm is the protons of CH in main chains and CH_3CO in DAAM side chain. The signals at 2.6-3.2 ppm is the protons of CH_2 in DAAM side chain.

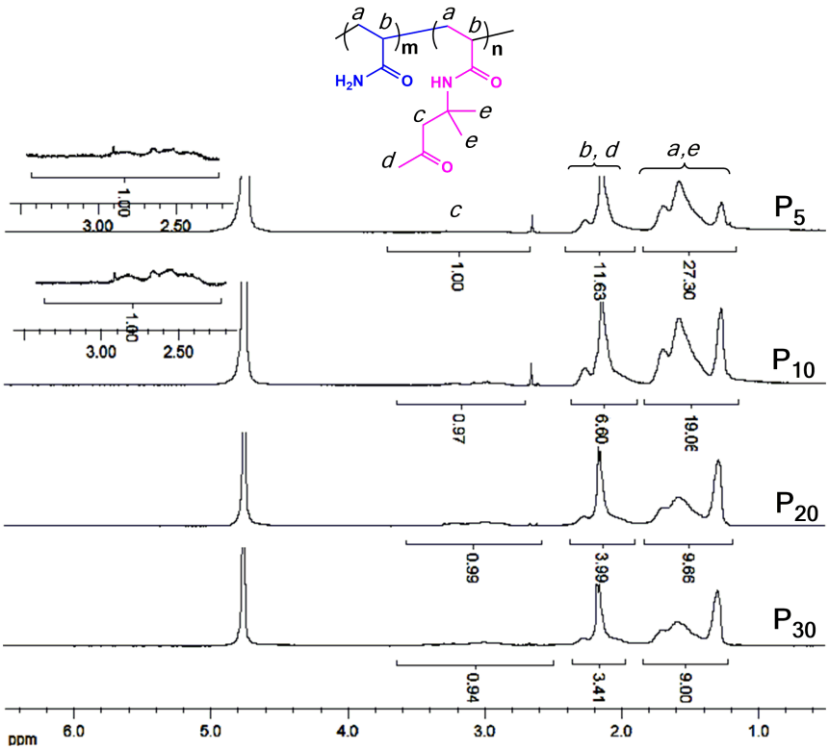

Fig. S1 ^{1}H NMR spectra of P_5, P_{10}, P_{20} and P_{30} in D_2O

Fig. S2 is the GPC chromatogram for the polymers.

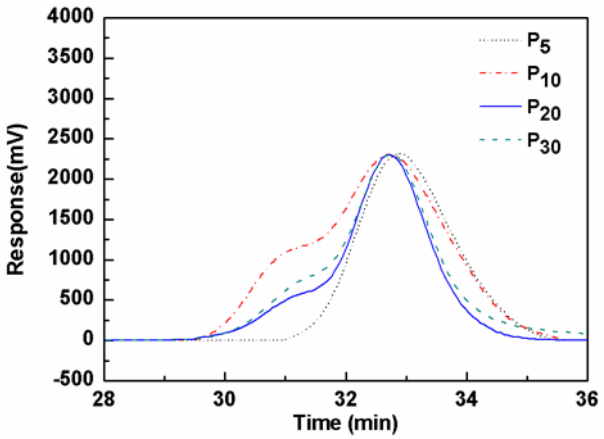

Fig. S2 GPC traces of precursor polymers

Fig. S3 is the images of hydrogels undergoing loading test. As shown in Fig. S3, the hydrogel of P_{30} and P_{20} can be loaded 100 g weight wihout breaks; comparably, the hydrogel of P_{10} and P_5 only can be loaded 50 g and 25 g weight with slight distorted shapes, respectively.

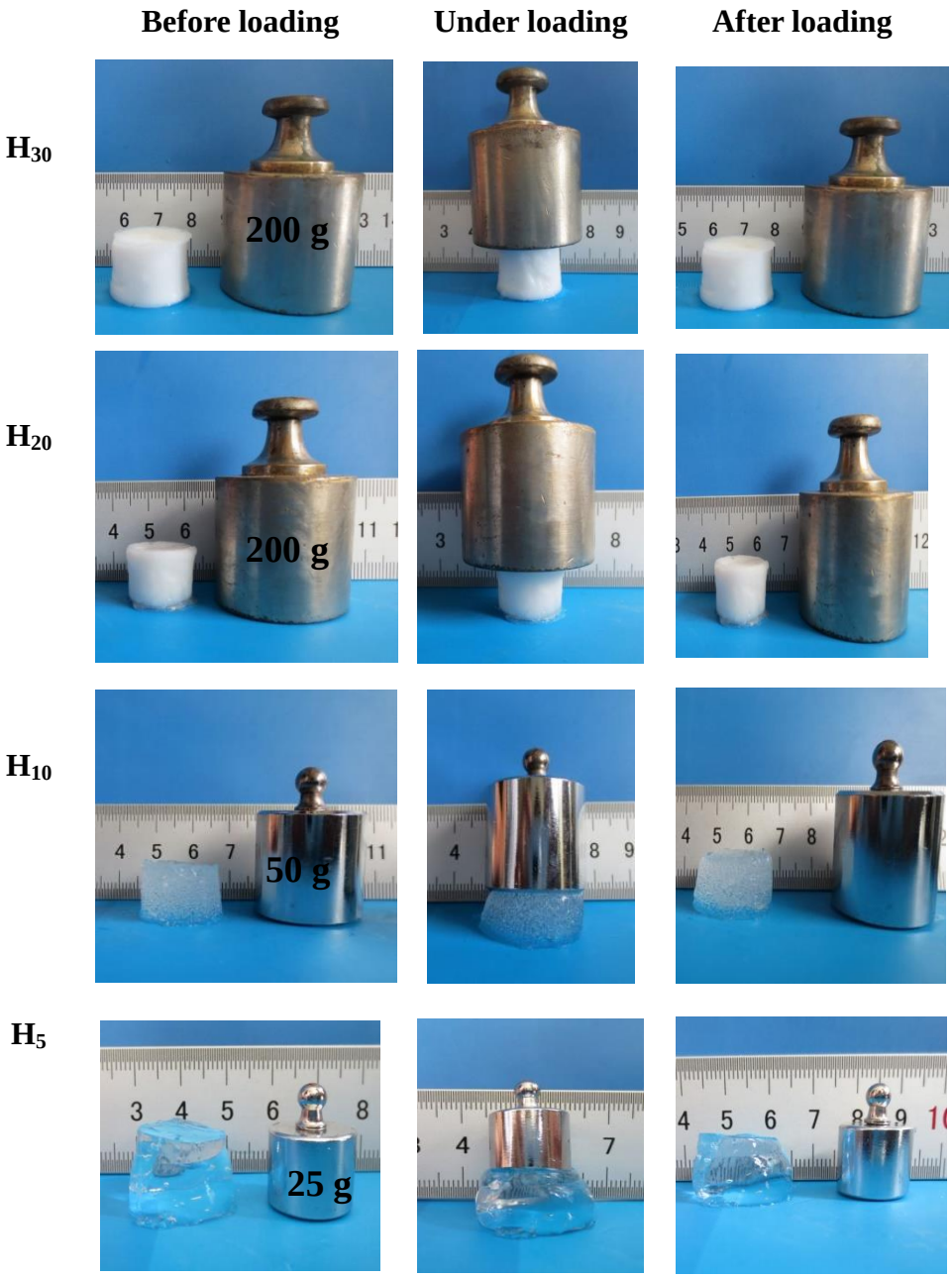

Fig. S3 Images of hydrogels with loading.

Fig. S4 is IR spectrum of DAAM, polymers and hydrogels. The polymers show stretching band for C=O at 1715 cm^{-1}, which is assigned to the characteristic absorptions of DAAM. Moreover, the strength of the band for C=O increase from P5 to P30, caused by the increasing of DAAM content. However, when ADH mixed with polymers to form hydrogels, the band at 1715cm^{-1} attributable to C=O of ketones disappeared, and concomitantly a new band at 1665cm^{-1} ascribed to C=N appeared.

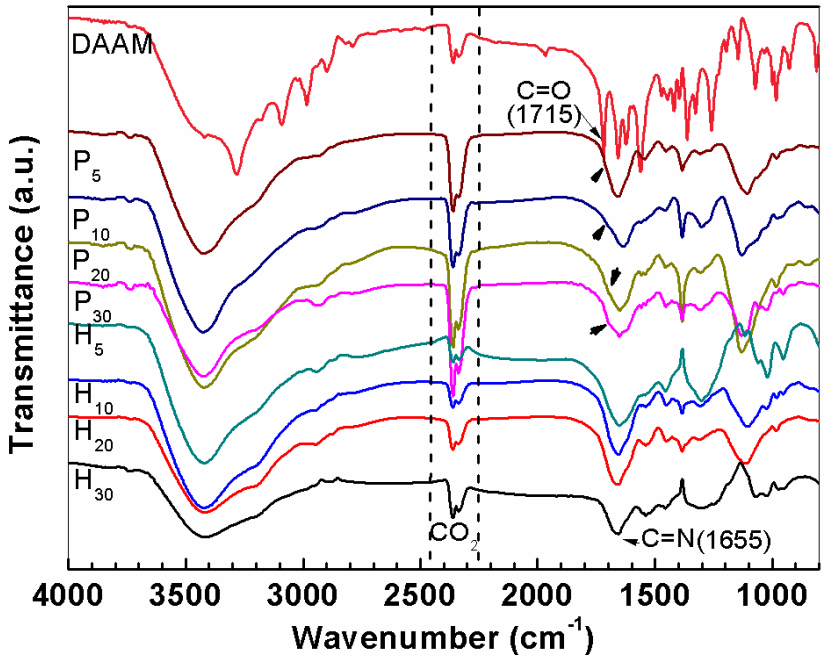

Fig. S4 IR spectrum of DAAM, polymers and hydrogels.

Fig. S5 is weight change (%) during the degradation process of gels in pH 7.4 and pH 2.5.

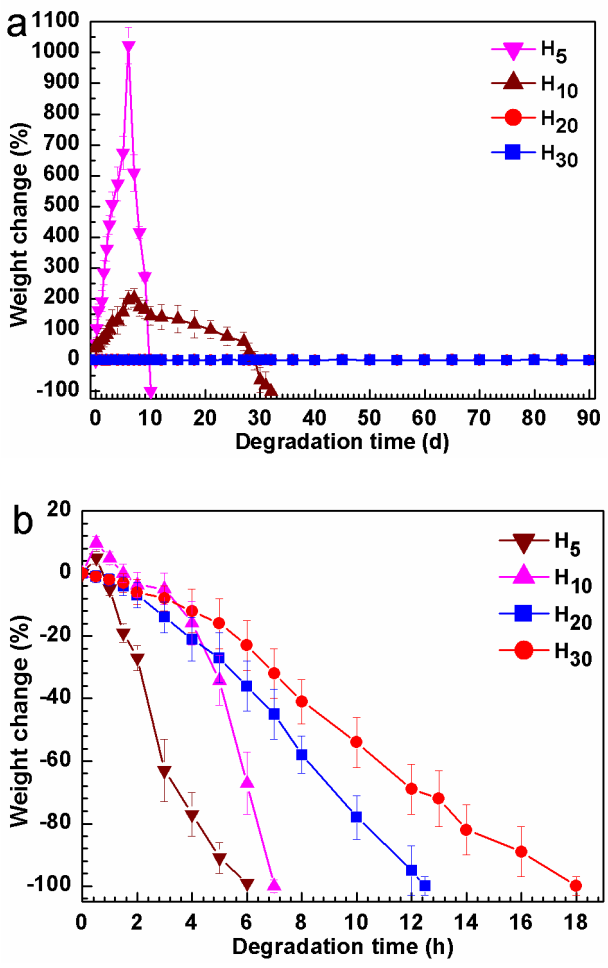

Fig. S5 Degradation of gel in pH 7.4 (a) and pH 2.5 (b) phosphate buffered saline (PBS).

Fig. S6 is the *in vitro* Rh B release profiles of Rh B -loaded $\mathbf{H_{20}}$, $\mathbf{H_{10}}$, and $\mathbf{H_5}$ at pH 2.5, 6.0 and 7.4.

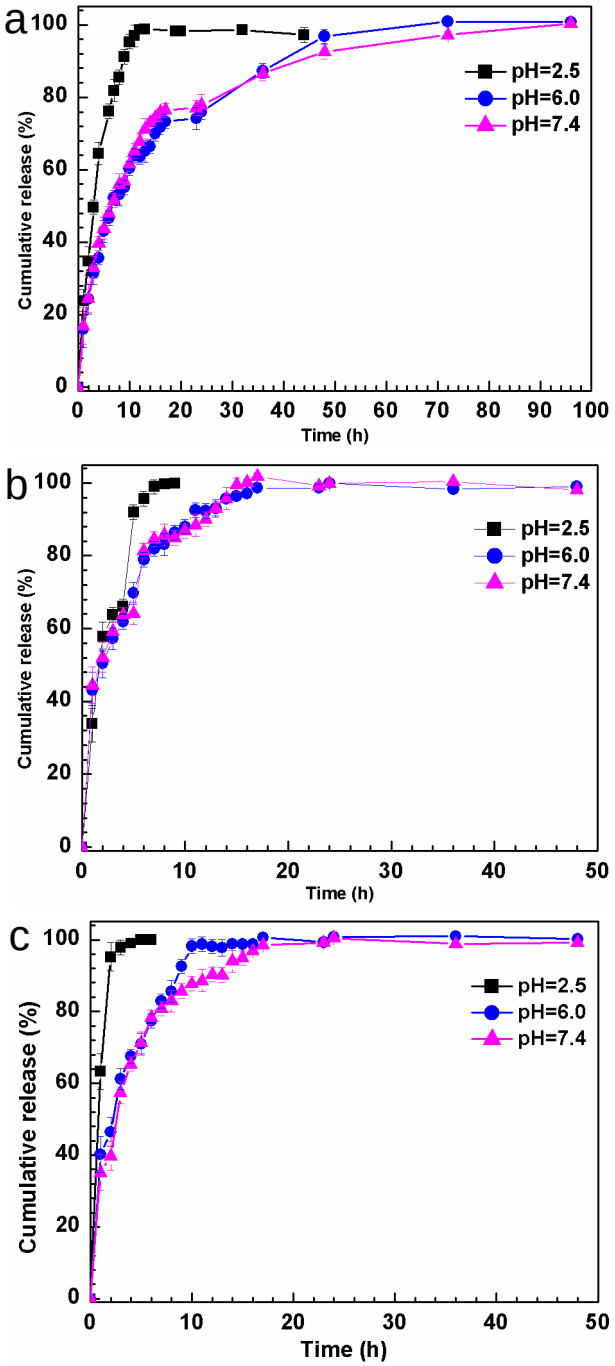

Fig. S6 *In vitro* Rh B release profiles of Rh B -loaded $\mathbf{H_{20}}$ (a), $\mathbf{H_{10}}$ (b), and $\mathbf{H_5}$ (c) at pH 2.5, 6.0 and 7.4.

Healing behavior of H_{20} and H_{30}

We tested self-healing properties of $\mathbf{H_{20}}$ and $\mathbf{H_{30}}$ at different pH (4.0, 5.0 6.0) and temperature (25 ^{o}C, 37 ^{o}C, 50 ^{o}C) with longer self-healing time (72 h). As shown in Fig. S7, S9, S11, S13, S15, S17, $\mathbf{H_{30}}$ and $\mathbf{H_{20}}$ did not exhibit self-healing behavior at pH 4.0, 5.0, 6.0 at 25 ^{o}C for 72 h. When the temperature increased to 37 ^{o}C, the gels did not undergo self-healing process at pH 4.0, 5.0, 6.0 for 36 h (Fig. S8, S10, S12,

S14, S16, S18). The gels did not exhibit self-healing behavior even at 50 °C. This may be attributed to that $\mathbf{H_{20}}$ and $\mathbf{H_{30}}$ are rigid and the gel cannot contact each other by simply putting together, resulting into the failure of self-healing behavior.

As $\mathbf{H_{20}}$ and $\mathbf{H_{30}}$ could not heal without any external intervention, we conclude that $\mathbf{H_{20}}$ and $\mathbf{H_{30}}$ did not exhibit self-healing ability.

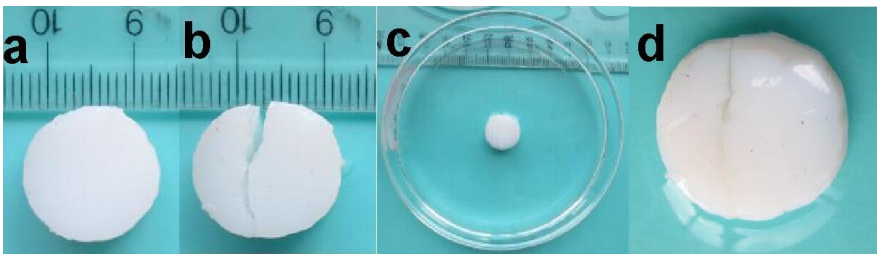

Fig. S7 Self-healing properties of $\mathbf{H_{30}}$ at pH 4.0: (a) original hydrogel, (b) hydrogelwas cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 4.0), (d) gel after healing for 72 h at 25 ℃ without any external intervention.

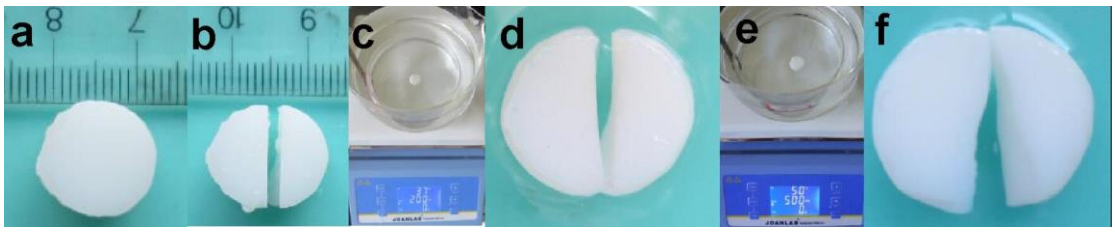

Fig. S8 Self-healing properties of $\mathbf{H_{30}}$ at 37 ℃ and 50 ℃ at pH 4.0: (a) original hydrogel, (b) hydrogel was cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 4.0, 37 ℃), (d) gel after healing for 36 h at 37 ℃ without any external intervention, (e) placed in 50 ℃ environment, (f) gel after healing for 36 h at 50 ℃ without any external intervention.

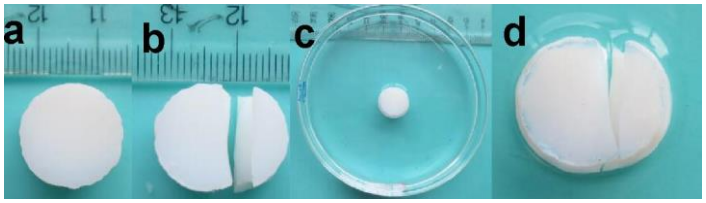

Fig. S9 Self-healing properties of $\mathbf{H_{30}}$ at pH 5.0: (a) original hydrogel, (b) hydrogelwas cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 5.0), (d) gel after healing for 72 h at 25 ℃ without any external intervention.

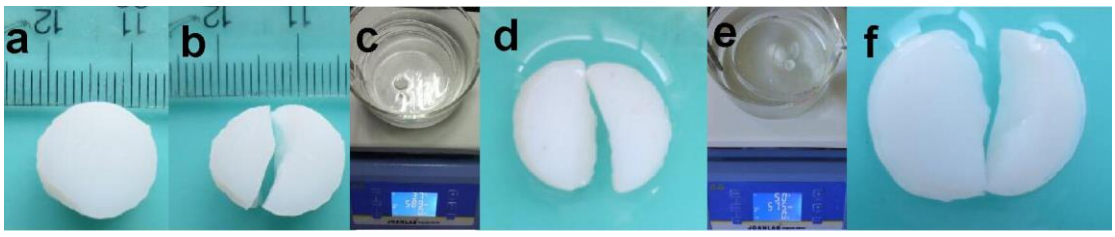

Fig. S10 Self-healing properties of $\mathbf{H_{30}}$ at 37 ℃ and 50 ℃ at pH 5.0: (a) original hydrogel, (b) hydrogel was cut into two pieces, (c) merged the gels by simply putting together and immersed it

in PBS (pH 5.0, 37 ℃), (d) gel after healing for 36 h at 37 ℃ without any external intervention, (e) placed in 50 ℃ environment, (f) gel after healing for 36 h at 50 ℃ without any external intervention.

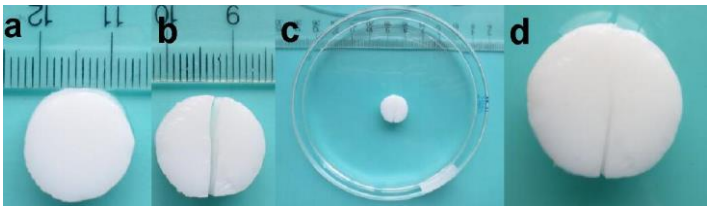

Fig. S11 Self-healing properties of $\mathbf{H_{30}}$ at pH 6.0: (a) original hydrogel, (b) hydrogelwas cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 6.0), (d) gel after healing for 72 h at 25 ℃ without any external intervention.

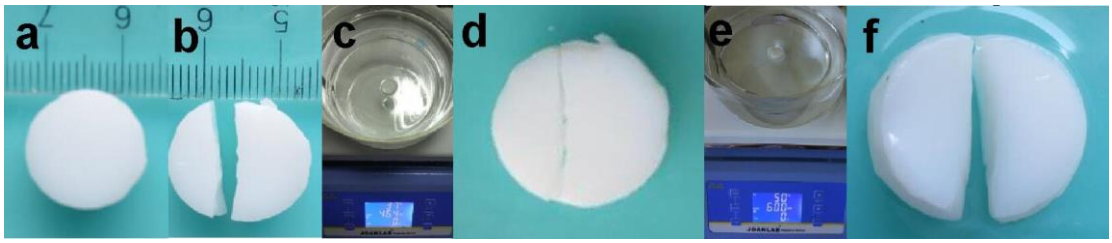

Fig. S12 Self-healing properties of $\mathbf{H_{30}}$ at 37 ℃ and 50 ℃ at pH 6.0: (a) original hydrogel, (b) hydrogel was cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 6.0, 37 ℃), (d) gel after healing for 36 h at 37 ℃ without any external intervention, (e) placed in 50 ℃ environment, (f) gel after healing for 36 h at 50 ℃ without any external intervention.

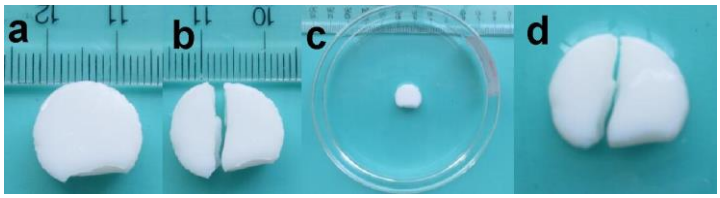

Fig. S13 Self-healing properties of $\mathbf{H_{20}}$ at pH 4.0: (a) original hydrogel, (b) hydrogelwas cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 4.0), (d) gel after healing for 72 h at 25 ℃ without any external intervention.

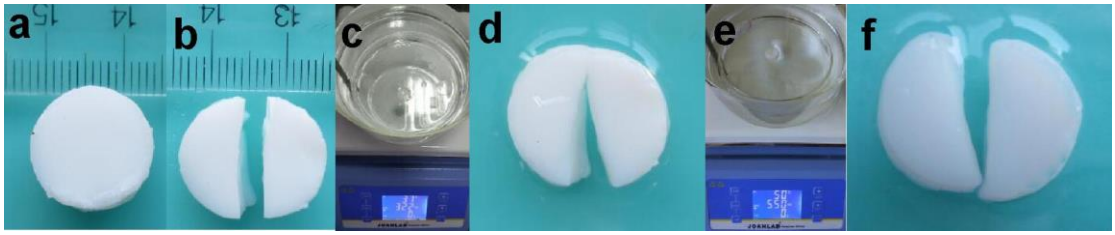

Fig. S14 Self-healing properties of $\mathbf{H_{20}}$ at 37 ℃ and 50 ℃ at pH 4.0: (a) original hydrogel, (b) hydrogel was cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 4.0, 37 ℃), (d) gel after healing for 36 h at 37 ℃ without any external intervention, (e) placed in 50 ℃ environment, (f) gel after healing for 36 h at 50 ℃ without any external

intervention.

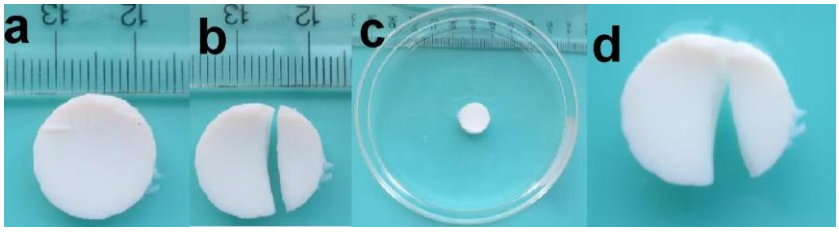

Fig. S15 Self-healing properties of $\mathbf{H_{20}}$ at pH 5.0: (a) original hydrogel, (b) hydrogelwas cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 5.0), (d) gel after healing for 72 h at 25 ℃ without any external intervention.

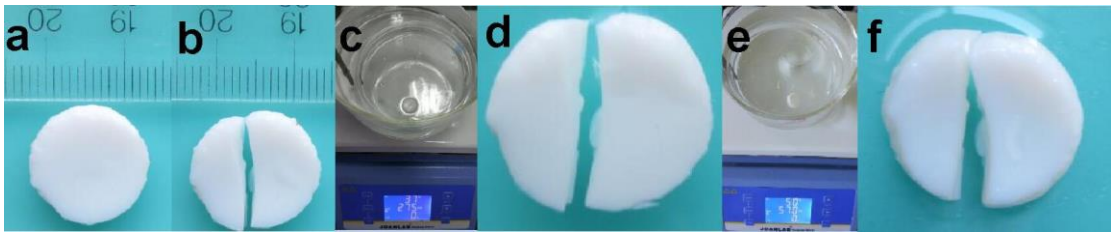

Fig. S16 Self-healing properties of $\mathbf{H_{20}}$ at 37 ℃ and 50 ℃ at pH 5.0: (a) original hydrogel, (b) hydrogel was cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 5.0, 37 ℃), (d) gel after healing for 36 h at 37 ℃ without any external intervention, (e) placed in 50 ℃ environment, (f) gel after healing for 36 h at 50 ℃ without any external intervention.

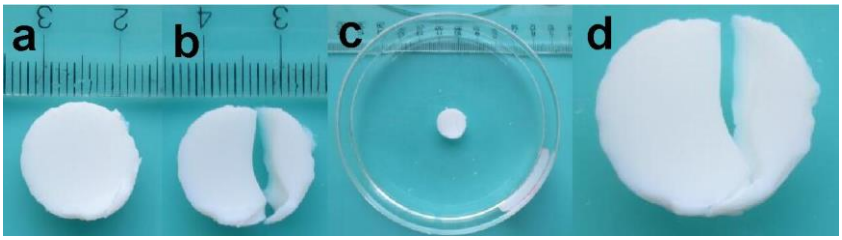

Fig. S17 Self-healing properties of $\mathbf{H_{20}}$ at pH 6.0: (a) original hydrogel, (b) hydrogelwas cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 6.0), (d) gel after healing for 72 h at 25 ℃ without any external intervention.

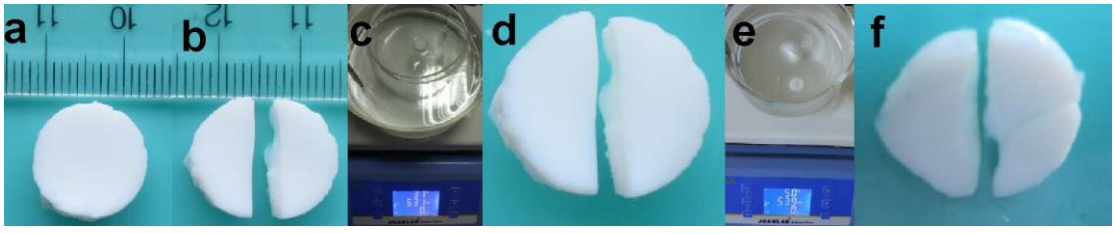

Fig. S18 Self-healing properties of $\mathbf{H_{20}}$ at 37 ℃ and 50 ℃ at pH 6.0: (a) original hydrogel, (b) hydrogel was cut into two pieces, (c) merged the gels by simply putting together and immersed it in PBS (pH 6.0, 37 ℃), (d) gel after healing for 36 h at 37 ℃ without any external intervention, (e) placed in 50 ℃ environment, (f) gel after healing for 36 h at 50 ℃ without any external

intervention.