Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Mechanically strong and tough hydrogels with pH-triggered self-healing and shape memory property based on dual physically cross-linked network

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Characterization.

Solution 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 or DMSO with a small amount of TMS as the internal reference standard. The fourier transform infrared (FTIR) spectra were recorded with a A225/Q Platinum ATR unit on a Bruker Tensor II spectrometer equipped with a RT-DLaTGS detector, at a scan speed of 1.6 kHz, 16 scans per sample and a resolution of 4 cm^{-1}. Ultraviolet spectra (UV, Shimadzu UV-2450 spectrophotometer).

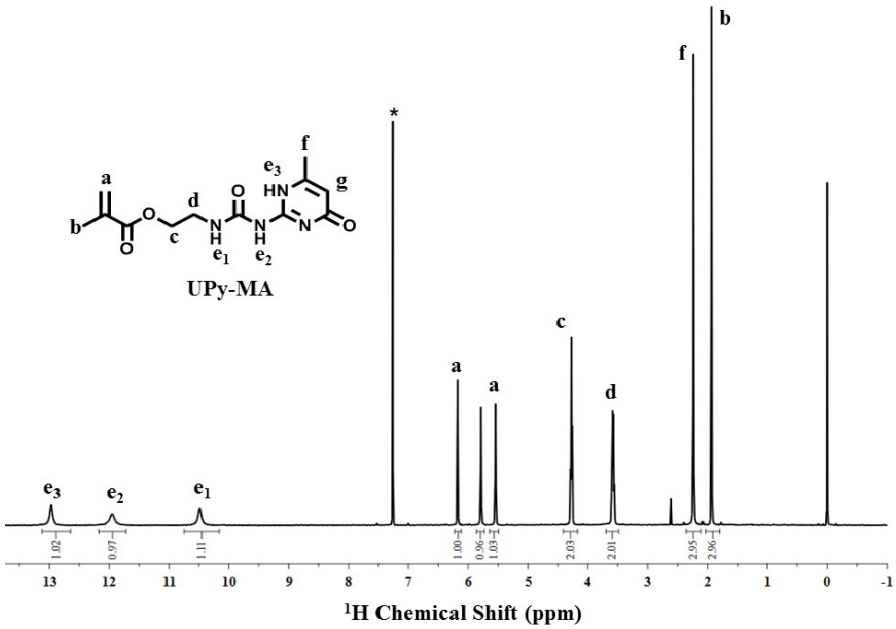

Figure S1. ^{1}H NMR spectrum of UPy-MA in $CDCl_3$. "*" indicates the proton signals of chloroform (δ_{iso}= 7.26 ppm) and TMS (δ_{iso}= 0 ppm). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.94 (s, 3H, CH_3), 2.24 (s, 3H, $ArCH_3$), 3.56-3.60 (m, 2H, $NHCH_2$), 4.26-4.29 (t, 2H, OCH_2), 5.53-5.55 (m, 1H, $C=CH_2$), 5.78 (s, 1H, aromatic ring), 6.18(s, 1H, $C=CH_2$), 10.49 (s, 1H, NH), 11.96 (s, 1H, NH), 12.97 (s, 1H, NH).

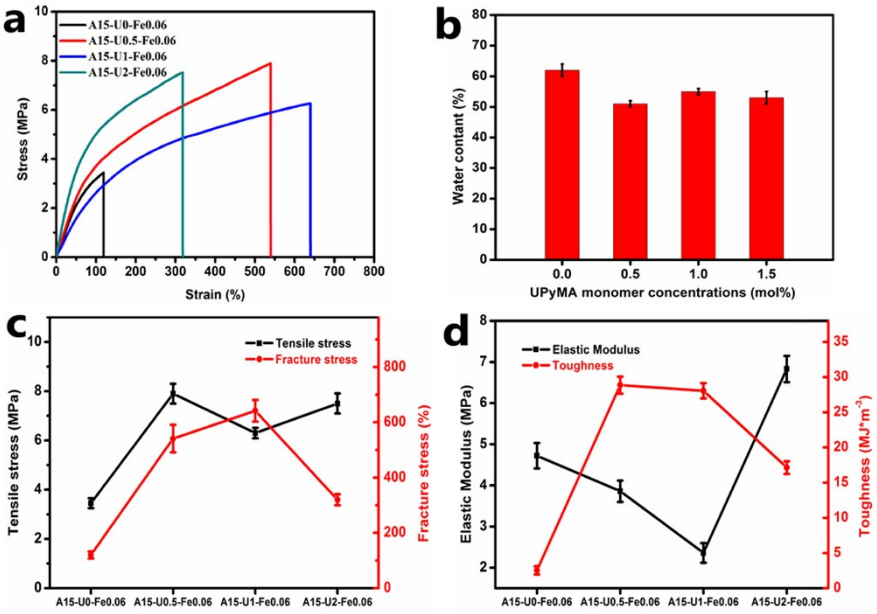

Figure S2. (a) Typical stress-strain profiles, (b) water contents, (c) tensile strength and elongation, and (d) elastic modulus and toughness of the D-hydrogels prepared with different UPyMA monomer concentrations. AM concentration = 7 mol L^{-1}, AA 15mol% of AM, Fe^{3+} concentration = 0.06 mol L^{-1}.

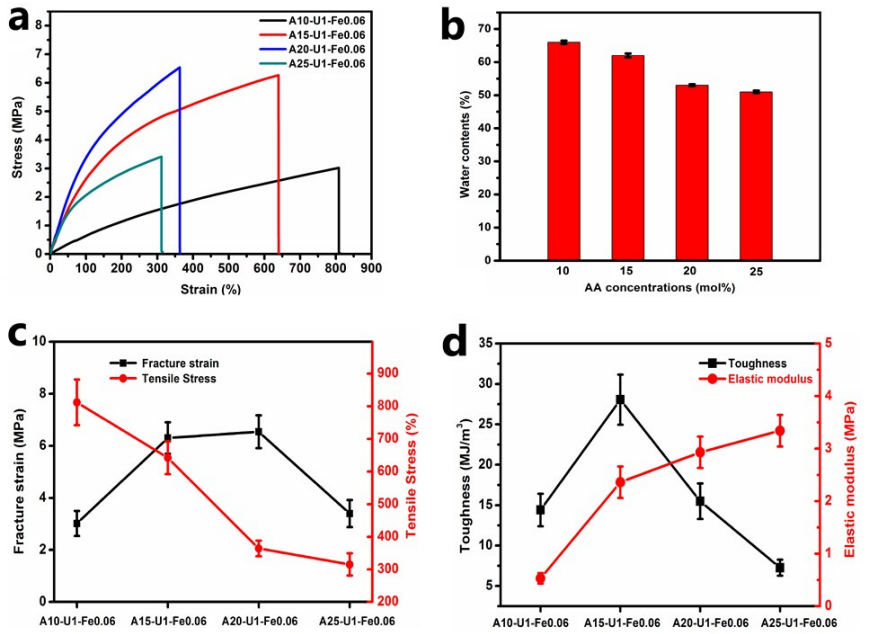

Figure S3. (a) Typical stress-strain profiles, (b) water contents, (c) tensile strength and elongation, and (d) elastic modulus and toughness of the D-hydrogels prepared with different AA concentrations. AM concentration = 7 mol L^{-1}, UPyMA 1mol% of AM, Fe^{3+} concentration = 0.06 mol L^{-1}.

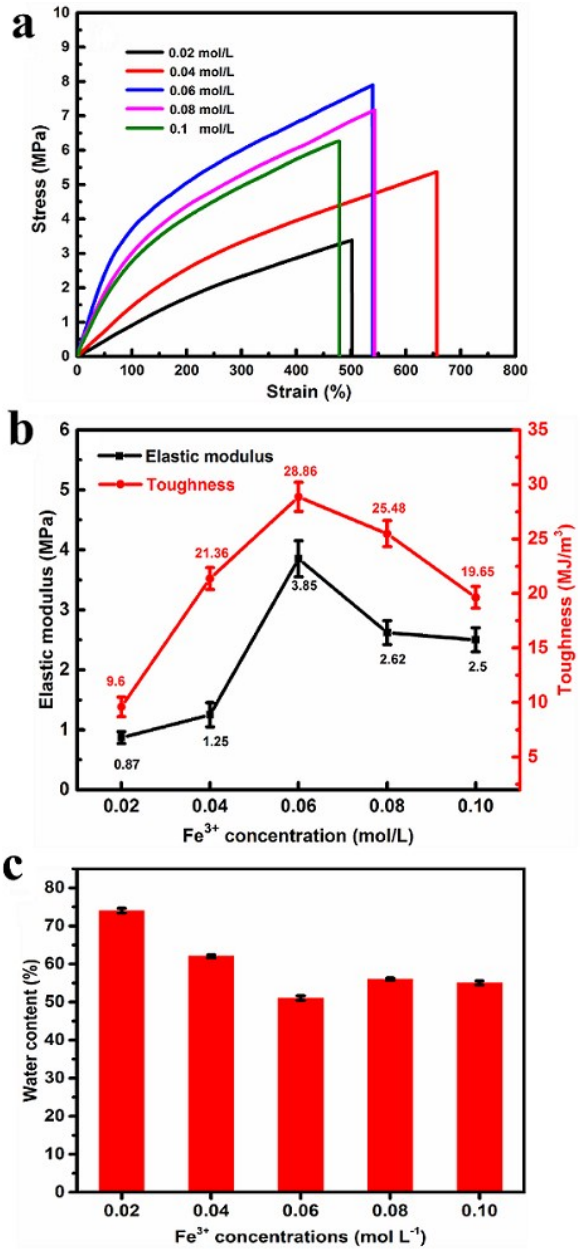

Figure S4. (a) Stress-strain profiles, (b) Elastic modulus and toughness and (c) water content of D-hydrogels at different Fe^{3+} concentrations. AM concentration = 7 mol L^{-1}, AA (15% molar ratio of AM), and UPyMA (1% molar ratio of AM).

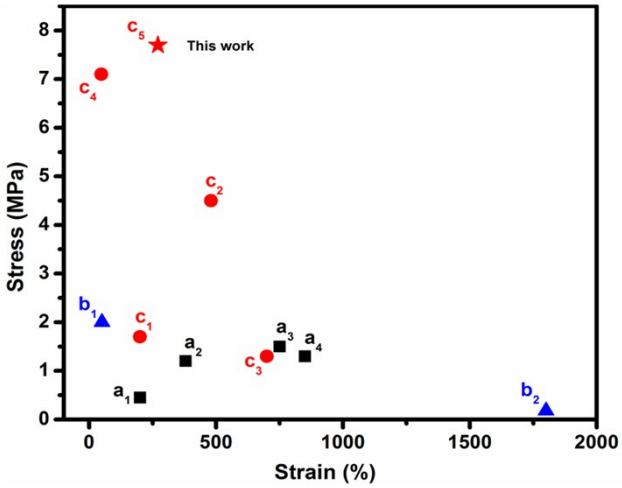

Figure S5. Comparison of the healing mechanical properties between the D-hydrogel and the previously reported self-healing hydrogel with the assistance of external stimuli, including **1)** heat, a_1 biphasic synergistic gel materials (BSGs)[1]; a_2 poly(N - acryloyl glycinamide) (PNAGA) physical hydrogel[2]; a_3 polyvinyl alcohol- poly (3,4-ethylenedioxythio–phene) :polystyrene sulfonate (PVA-PEDOT:PSS) physical hydrogel[3]; a_4 poly(acrylic acid)- cetyltrimethylammonium (PAA-CTA) physical hydrogel[4]; **2)** light irradiation, b_1 poly(N-acryloyl 6-aminocaproic acid)- functionalized gold nanoparticles (PA6ACA-functionalized AuNPs) physical hydrogel[5]; b_2 graphene oxide (GO)-hectorite clay-poly(N,N-dimethylacrylamide) (PDMAA) physical hydrogel[6]; **3)** pH triggering, c_1 sodium alginate/poly(acrylamide – co-acrylic acid)/Fe^{3+} (SA/P(AM-co-AA)/Fe^{3+}) physical hydrogel[7]; c_2 poly(acrylamide-co-acrylic acid)/Fe^{3+} (P(AM-co-AA)/Fe^{3+})[8]; c_3 poly(acrylamide- co-acrylic acid-co-2-Vinyl-4,6-Diamino-2-vinyl-1,3,5-triazine)/Fe^{3+} ((PAM-co-AA- co-VDT)/Fe^{3+}) physical hydrogel[9]; c_4 P(AM-co-AA)/Na-Alginate/ Fe^{3+} physical Hydrogels[10]; c_5 PAM-co-AA-co-UPy-MA/ Fe^{3+} physical hydrogel in this work.

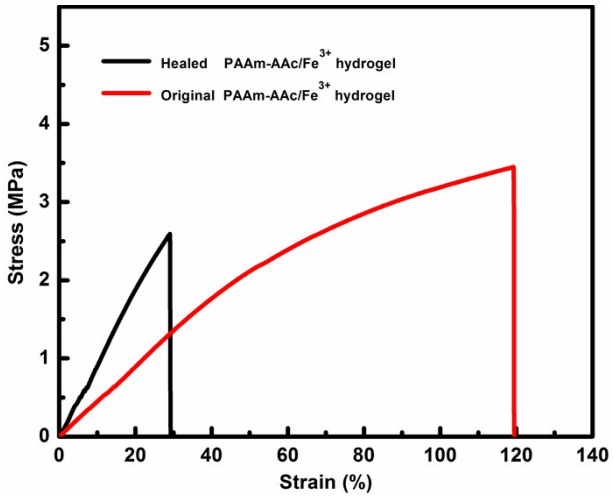

Figure S6. Stress−strain curves of the origin and healed D-hydrogel specimen A15-U0-Fe0.06 (the pristine PAM-AA/Fe^{3+} hydrogel without UPy-monomer).

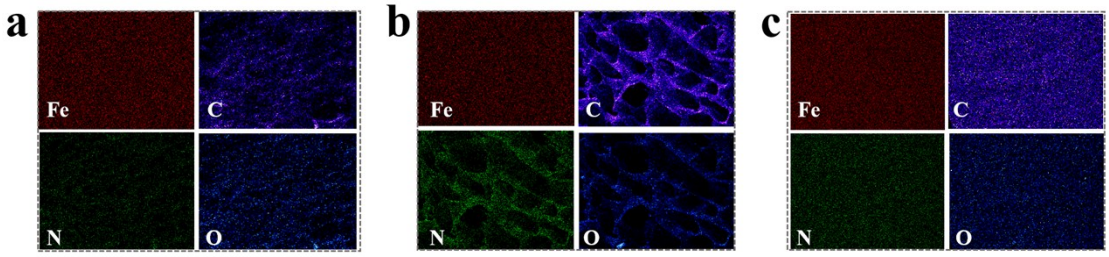

Figure S7. EDS images elemental maps for freeze-dried A15-U1-Fe0.06 hydrogel. (a) Original sample, (b) alkaline treatment sample, and (c) healed sample.

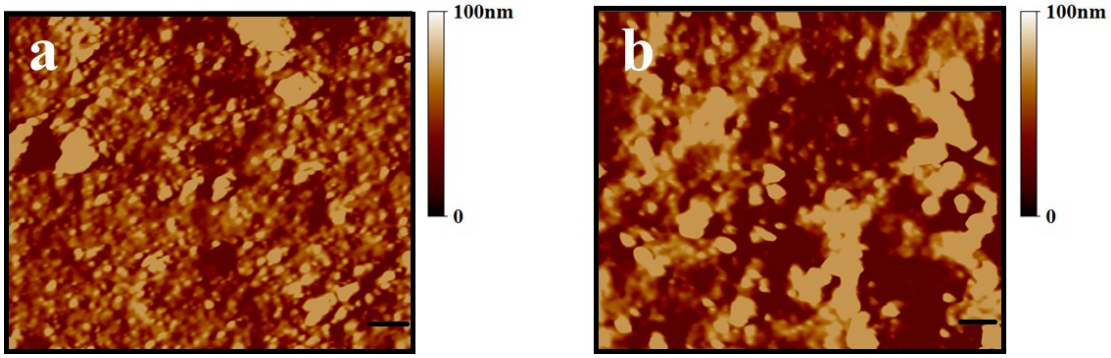

Figure S8. AFM images of freeze-dried A15-U0-Fe0.06 (a) and A15-U1-Fe0.06 (b) with scale bars of 1 μm.

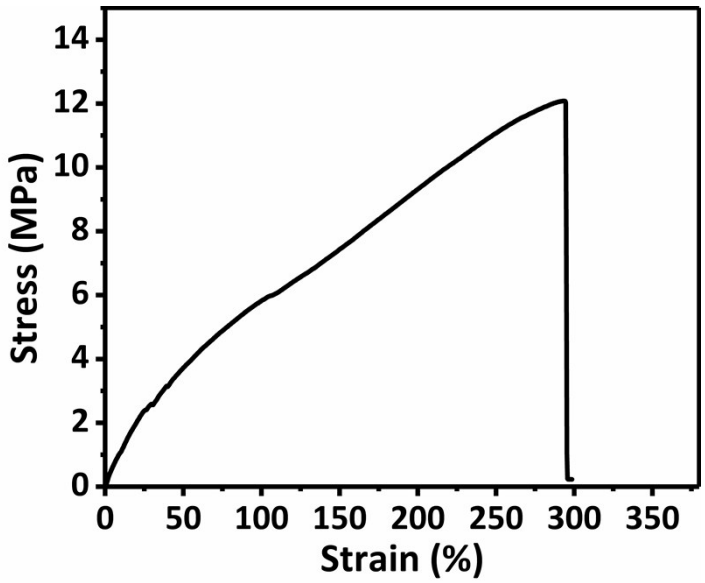

Figure S9 Stress-strain curve of D-hydrogel treated in 0.06M $Fe(NO_3)_3$ solution for 5 hours and then soaked in deionized water for 24 hours.

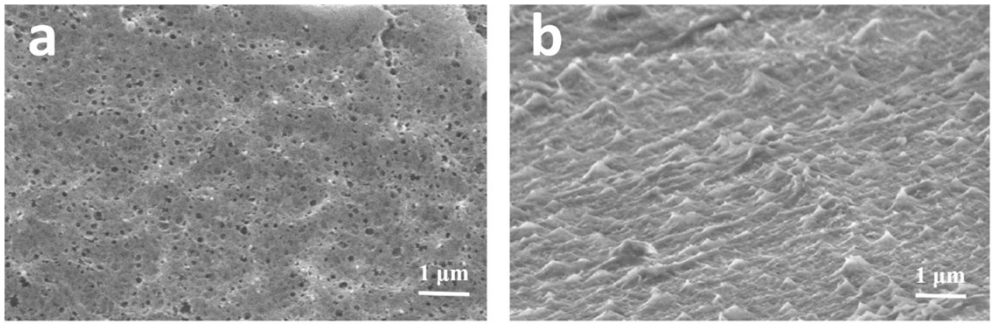

Figure S10 SEM images of as-prepared S-hydrogel (a) and D-hydrogel (b)

Table S1 Atomic content of main elements of S-hydrogel (A15-U1-Fe0.06) obtained from EDS

Element	Atomic content (%)
C	64.04
N	4.94
O	24.30
Fe	6.72

References

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