Chemistry of Materials

Supporting Information

Stimuli-responsive supramolecular hydrogels with high extensibility and fast self-healing via pre-coordinated mussel-inspired chemistry

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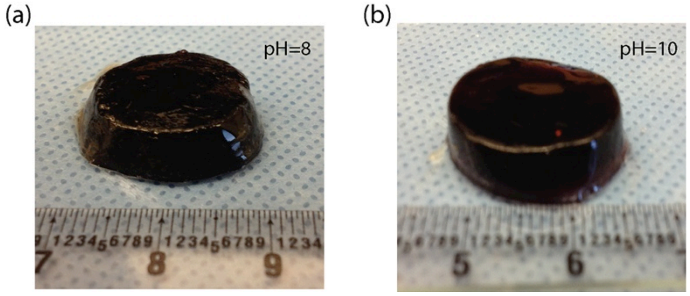

Figure S1. Hydrogels fabricated using bis- (a) and tris-complexes (b) of catechol-Fe^{3+} as crosslinkers. The concentration of $FeCl_3$ is 0.019 wt% for both hydrogels. Note that the former hydrogel formed at pH8 is not able to maintain the shape due to its lower elastic modulus.

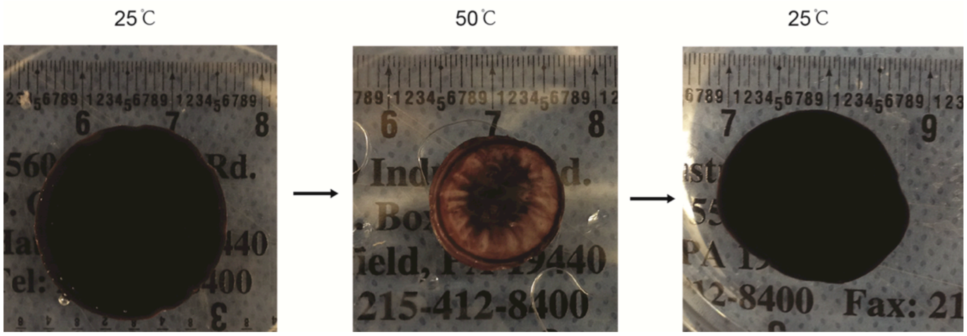

Figure S2. Thermo-responsive PCCI-crosslinked poly(N-isopropylacrylamide) hydrogel. The hydrogel undergoes pronounced shrinkage and color change after being heated to 50℃. The size and color changes are reversible in response to temperature change.

Table S1. Compositions of the PCCI crosslinked polyacrylamide hydrogels. Molar ratio between DMA and Fe^{3+} is 3:1 and the pH is 10.

Name	$FeCl_3$ (wt%)	DMA (wt%)	Acrylamide (wt%)	DMSO (v%)	LAP (wt%)
0.5xFe	0.019	0.088	14	5	0.5
1xFe	0.038	0.176	14	5	0.5
2xFe	0.076	0.352	14	5	0.5

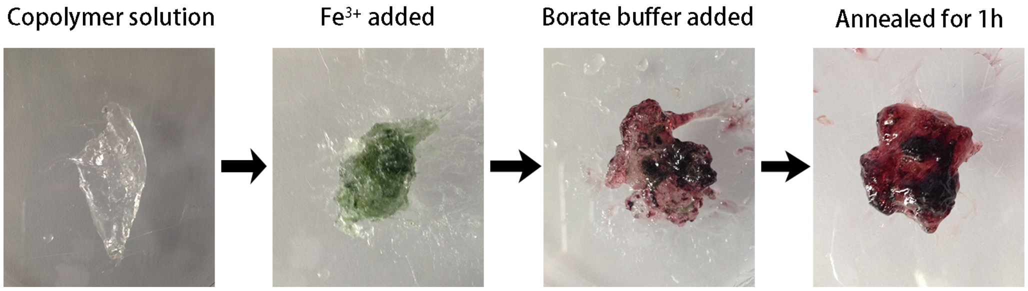

Figure S3. Fabrication of catechol-Fe^{3+} based polyacrylamide hydrogel via mixing and pH jump method. The hydrogel prepared with this method displays pronounced heterogeneities even after being annealed for 1 h.

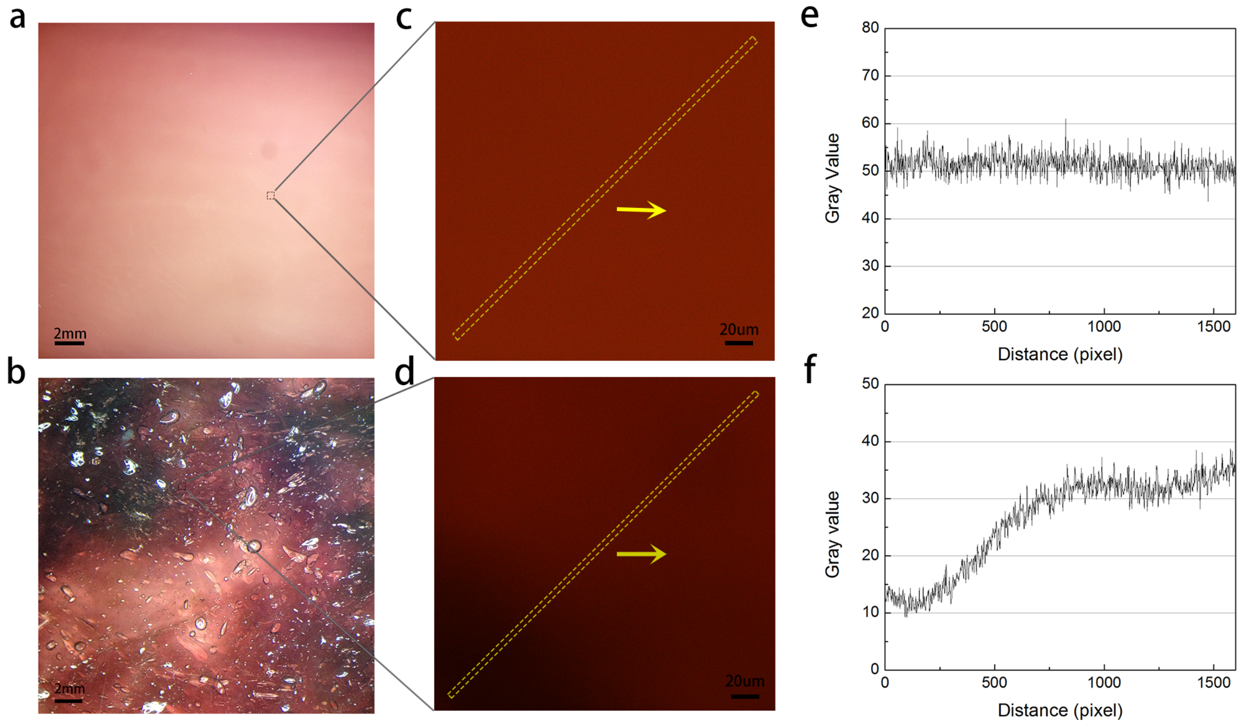

Figure S4 Microscopic image of hydrogels prepared using the pre-coordination method and pH jump method. Figure (a) and (c) are optical microscopic images of hydrogel prepared using the pre-coordination method; figure (b) and (d) are optical microscopic images of hydrogel using the pH jump method. Figure (e) and (f) are gray scale plots along the diagonals of (c) and (d) using the ImageJ software (NIH, 1.49v). The pre-coordination method produced a hydrogel with homogeneous microstructure (Figure a, c, e), while pH jump method produced a large degree of heterogeneity and many defects in the hydrogel (Figure b, d, f). Hydrogel thickness=1.5mm.

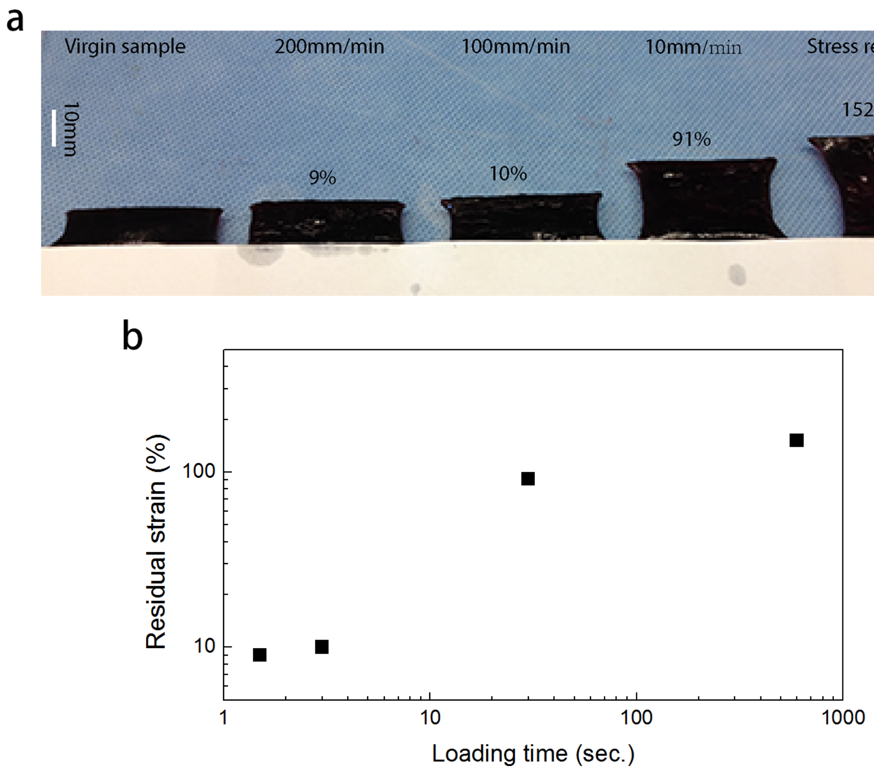

Figure S5. Images of un-stretched hydrogel and hydrogel samples recovered after being stretched to 5 times their original length under various conditions. (a) Hydrogels stretched under different loading rates (200 mm/min, 100 mm/min, 10 mm/min) and stress relaxation condition for 10 minutes resulted in residual strains of 9%, 10%, 91% and 151% respectively. (b) Correlation between the residual strain and the loading times of 1.5 s, 3.0 s, 30 s, 600 s (for 200mm/min, 100mm/min, 10mm/min and stress relaxation) shows that longer loading times resulted in larger residual strains.

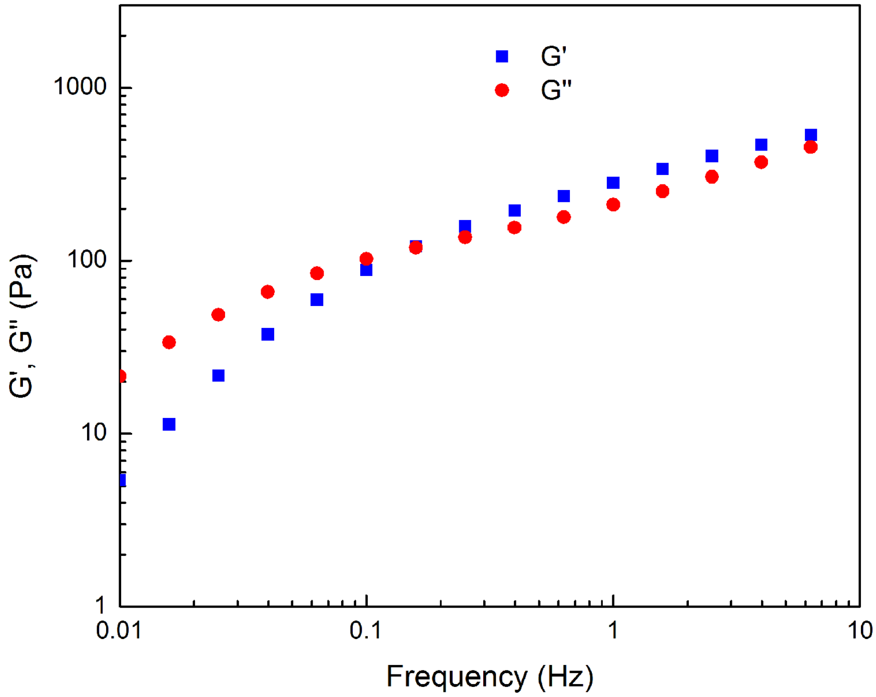

Figure S6. Dynamic moduli of 0.5xFe hydrogel under varied frequencies. The sol-gel transition occurs at 0.16Hz.

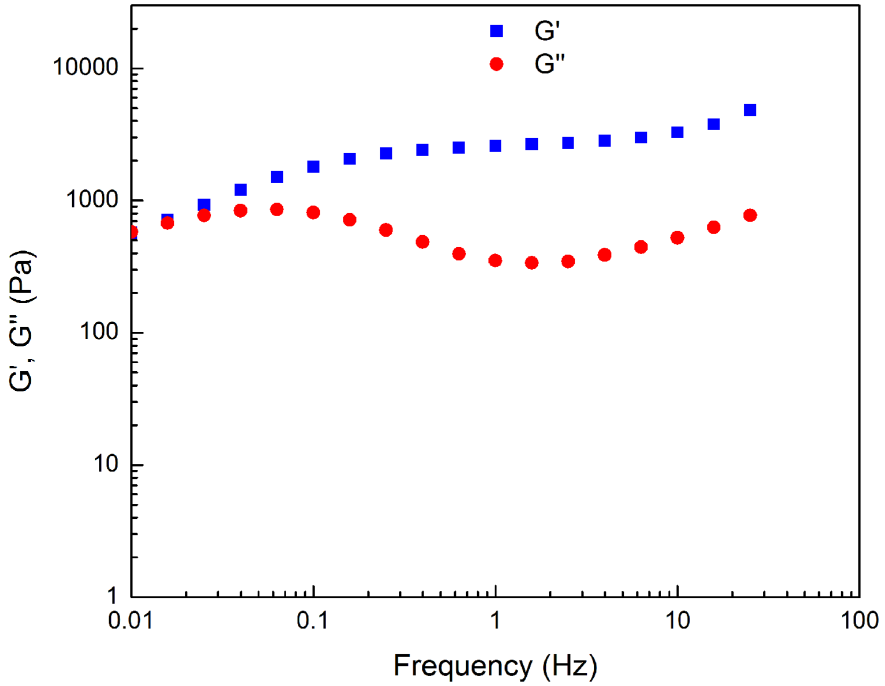

Figure S7. Dynamic moduli of 2xFe hydrogel under varied frequencies. The sol-gel transition occurs at 0.016Hz.

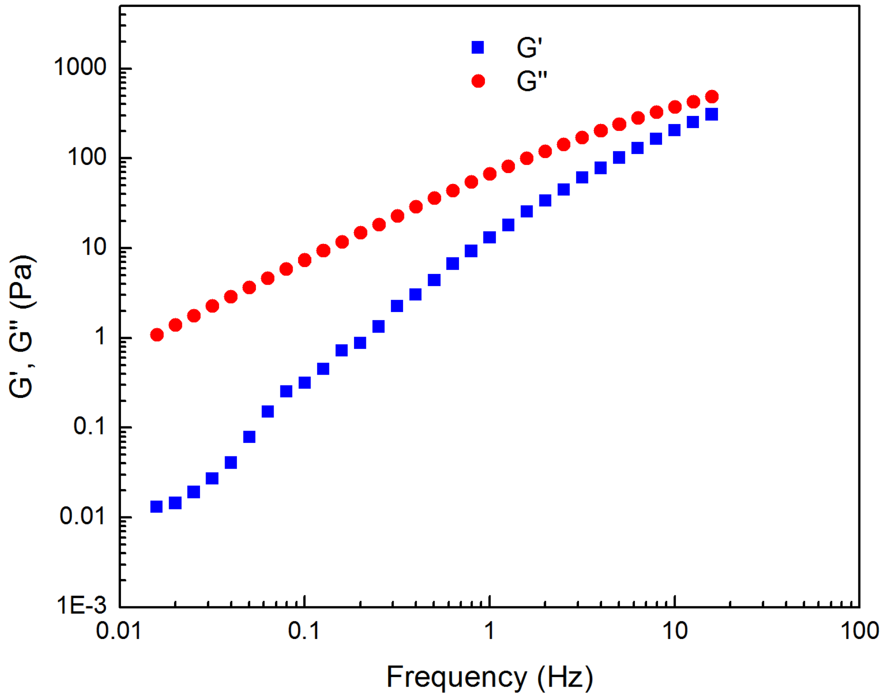

Figure S8. Dynamic moduli polyacrylamide solution with no crosslinker under varied frequencies. The elastic modulus is lower than the loss modulus in the full frequency range, indicating that the uncrosslinked PAAM is essentially a viscous liquid.

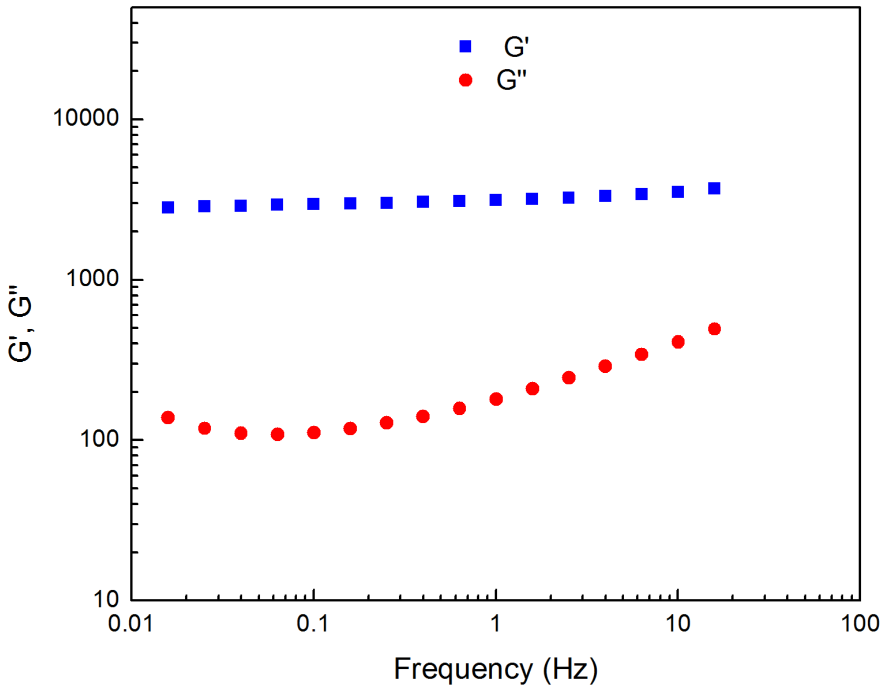

Figure S9. Dynamic moduli of covalent polyacrylamide hydrogel under varied frequencies. The elastic modulus remains constant in the full frequency range, indicating that the covalent PAAM hydrogel is elastic in the entire tested frequency range.

Experimental Section

Synthesis and thermo-responsive property of poly(N-isopropylacrylamide)-based hydrogel. Poly(N-isopropylacrylamide) based hydrogel was fabricated using the same method as in the fabrication of PCCI cross-linked polyacrylamide hydrogel. To minimize the irradiation-induced temperature increase, the light bulb and the precursor solution was kept 50 cm apart. To testify the thermo-responsivity of the hydrogel, a disc-shaped hydrogel was first immersed in borate buffer (0.1M, pH 10.2) at ambient temperature. Then the hydrogel was transferred to an oven set at 50℃ for 30 minutes. Thermo-responsive property of the hydrogel was validated by the color change and volume collapse at the higher temperature. The thermo-induced color change and volume collapse was reversed when it was cooled to ambient temperature.

Synthesis of catechol-Fe^{3+} based polyacrylamide hydrogels by mixing-induced gelation. The concentrations of all the reagents used in this method were the same as in the pre-coordination method. In the first step, poly(AAM-DMA) solution was prepared by photo-polymerization of the monomers in aqueous solution. 7.5 ml of the stock acrylamide solution was pipetted into a 50 ml flask followed by the addition of 3.7 ml de-ionized water. The acrylamide solution was bubbled with nitrogen for 10 minutes. Then DMA and LAP in DMSO (35.2 mg DMA and 100mg LAP in 1ml DMSO) were added to the de-oxygenated solution. The flask was vacuumized with oil pump and refilled with N_2 for 3 times to eliminate the oxygen. The UV-induced polymerization was carried out in the sealed flask for 10 minutes. About 1 ml of the irradiated solution was taken out and placed on a glass slide. $FeCl_3$ stock solution (33 ul) was pipetted into the copolymer solution and mixed vigorously to form catechol-Fe^{3+} mono-complex. Gelation was then induced by the addition of 150mM borate buffer (606 μl) and vigorous mixing. After mixing for about 2 minutes, the hydrogel was annealed at room temperature for 1 hour.

Optical microscopic investigation of the hydrogel microstructure. UV-crosslinked PCCI-based hydrogel for microscopic investigation was prepared with parallel glass plates with a 1.5mm spacer. The hydrogel by pH jump was firstly prepared as in the above procedure and then compressed with parallel glass plates to 1.5mm thick. The hydrogels in the glass molds were investigated with an optical microscope (SMZ660, Nikon, Japan). The gray values of the images were obtained by first transforming the images to gray scale images and measuring the gray values with a software (ImageJ 1.49v, NIH).

Synthesis of non-crosslinked and covalently-crosslinked polyacrylamide hydrogel. The concentration of acrylamide was kept 14 wt% for both non-crosslinked and covalently crosslinked polyacrylamide. N,N'-Methylene bisacrylamide was used as the covalent crosslinkers and the concentration was 0.034 wt%, which has the same molar concentration with $FeCl_3$ in 1xFe hydrogel. The concentration of the photo-initiator (LAP) was 0.1 wt%.