

Support Information

A pH-induced self-healable shape memory hydrogel with metal-coordination cross-links

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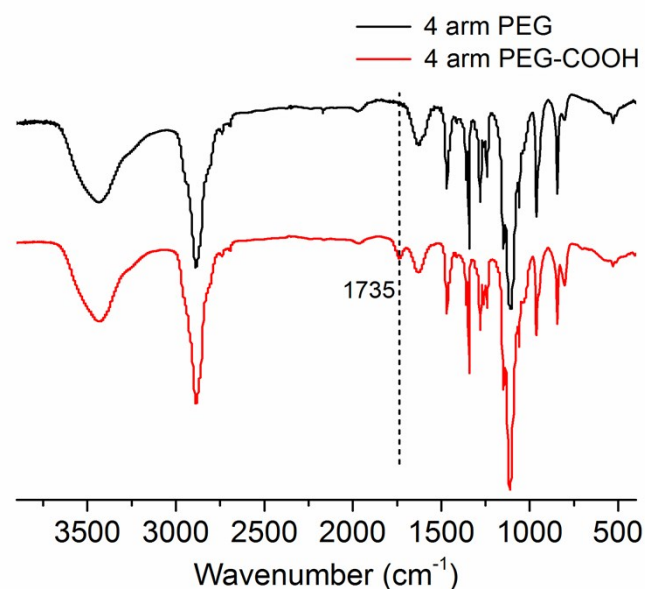


Figure S1. FT-IR spectra of 4 arm PEG and 4 arm PEG-COOH.

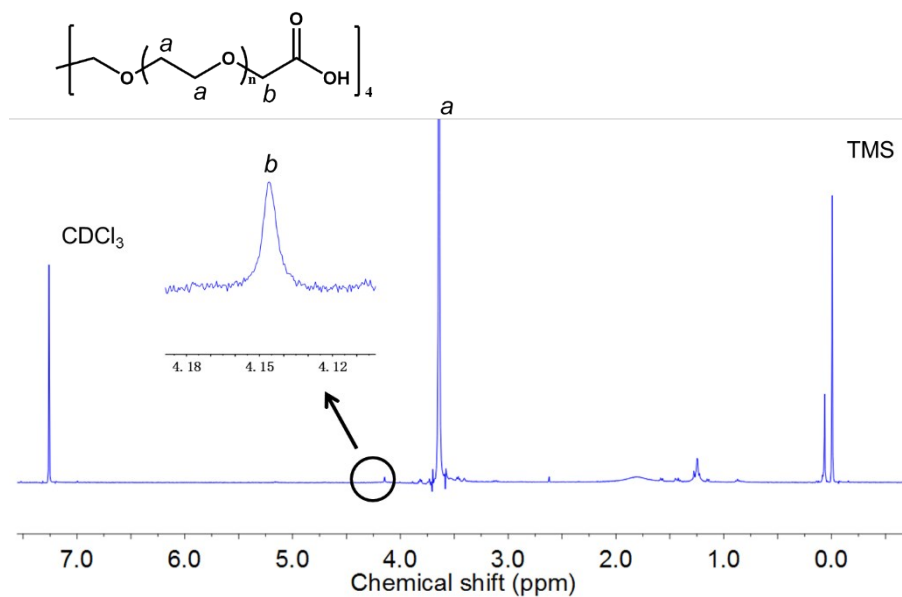


Figure S2. ¹H NMR spectrum of 4 arm PEG-COOH in CDCl₃.

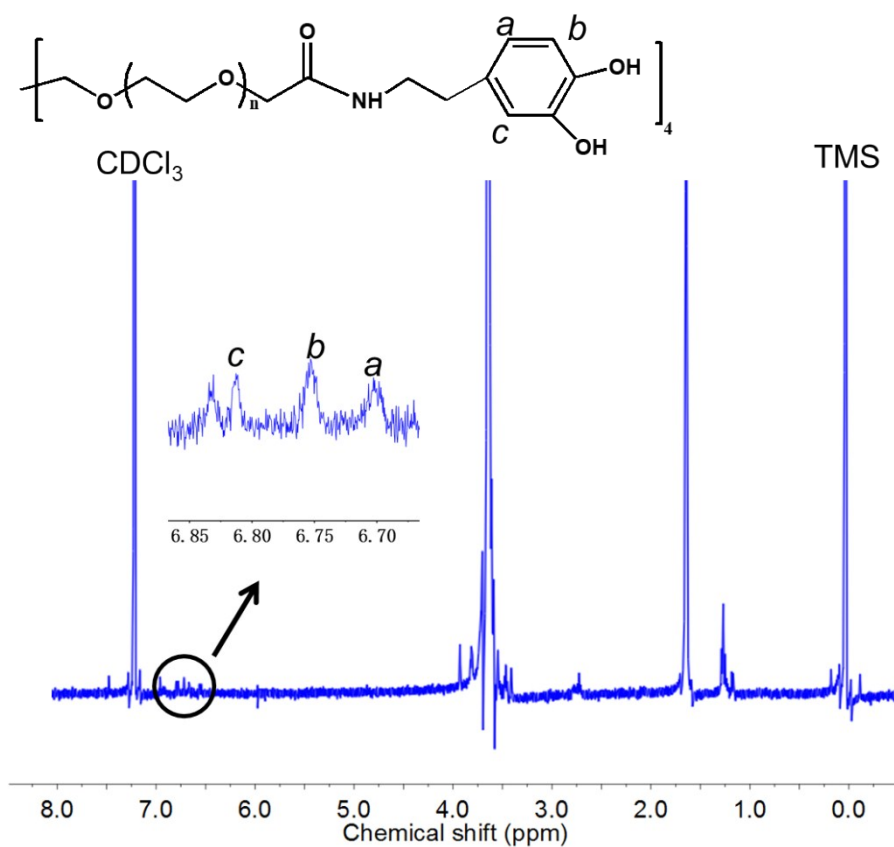


Figure S3. ¹H NMR spectrum of 4 arm PEG-DA in CDCl₃.

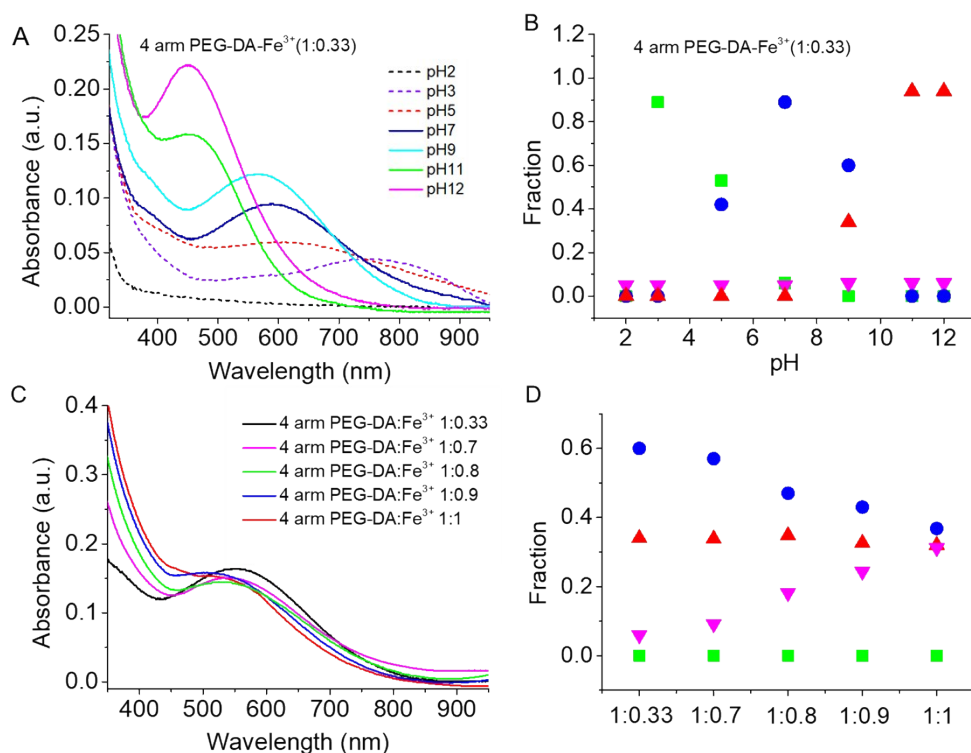


Figure S4. (A) UV-vis spectra of 4 arm PEG-dopa-Fe³⁺ solution at pH values of 2, 3, 5, 7, 9, 11 and 12. The concentration of 4 arm PEG-dopa was 2.5 mg/mL and the molar ratio of dopa: Fe³⁺ is 1:0.33. Absorption maxima for pure mono-(~751 nm), bis- (~574 nm), and tris-catecholato-Fe³⁺ (~498 nm) complexes. (B) The relative fractions of the three catechol-Fe³⁺ complexes calculated from the corresponding specific absorbance peaks: mono- (■), bis- (●), and tris-catechol-Fe³⁺ (▲) complexes, catechol-catechol covalent bond (▼). (C) UV-vis spectra of 4 arm PEG-dopa-Fe³⁺ solution with the Fe³⁺:dopa molar ratio of 1:0.33, 1:0.7, 1:0.8, 1:0.9 and 1:1, respectively. (D) The relative fractions of the three catechol-Fe³⁺ complexes calculated from the corresponding specific absorbance peaks: mono- (■), bis- (●), and tris-catechol-Fe³⁺ (▲) complexes, catechol-catechol covalent bond (▼).

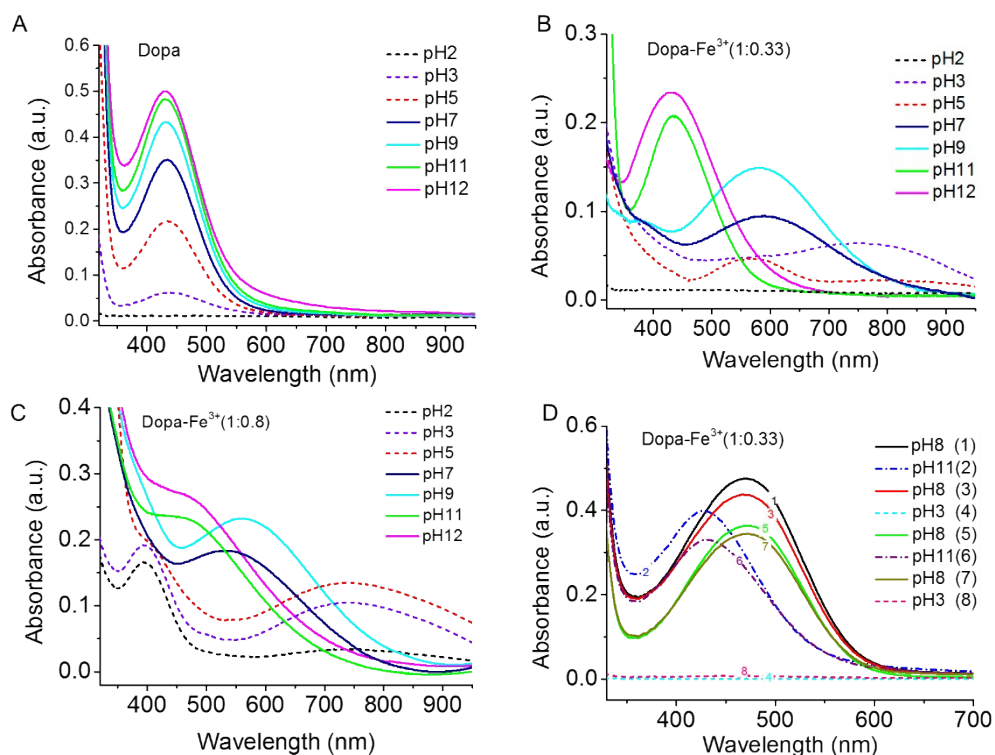


Figure S5. UV-vis spectra of dopa solution (A) and dopa-Fe³⁺ solution (B) at pH values of 2, 3, 5, 7, 9, 11 and 12. The concentration of dopa solution was 0.01 mg/mL and the dopa: Fe³⁺ molar ratio was 3:1. Absorption maxima for pure mono-(~751 nm), bis-(~574 nm), and tris-catechol-Fe³⁺ (~498 nm) complexes. (C) UV-vis spectra of dopa-Fe³⁺ solution with the dopa: Fe³⁺ molar ratio of 1:0.8 at pH values of 2, 3, 5, 7, 9, 11 and 12. Absorption maxima for pure mono-(~751nm), bis- (~574 nm), and tris-catechol-Fe³⁺ (~498 nm) complexes, catechol-catechol covalent bond (~400 nm). (D) The UV-vis spectra of dopa-Fe³⁺ solution, in which the bis- (~574 nm), and tris-catechol-Fe³⁺ (~498 nm) complexes alternately change with cyclically changing pH value.

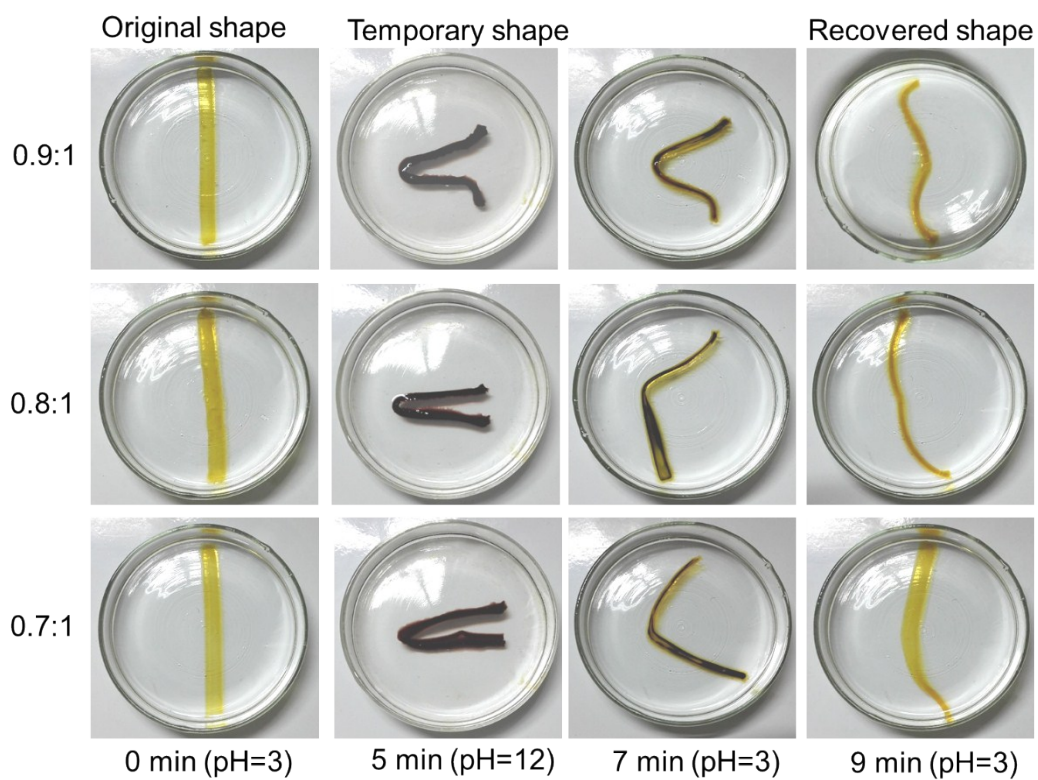


Figure S6. The photographs showing shape-memory behaviors of 4 arm PEG-dopa- Fe^{3+} hydrogels with dopa: Fe^{3+} molar ratios of 1:0.9, 1:0.8 and 1:0.7.

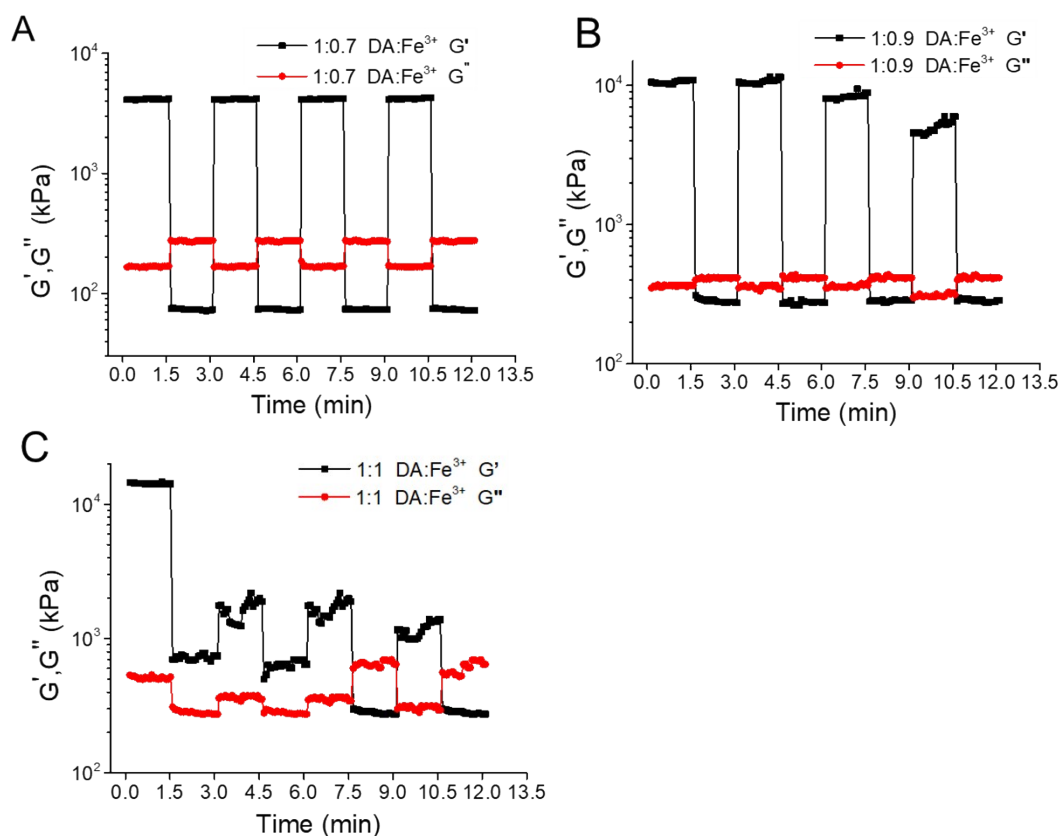


Figure S7. The rheological measurements of 4 arm PEG-dopa-Fe³⁺ hydrogels with dopa: Fe³⁺ molar ratios of 1:0.9 (A), 1:0.8 (B) and 1:0.7 (C), respectively. Alternate switched strains of small strain ($\gamma = 10.0\%$) and large strain ($\gamma = 3000\%$) at a fixed angular frequency (10 rad/s) were used, and each strain interval was kept for 90 s.

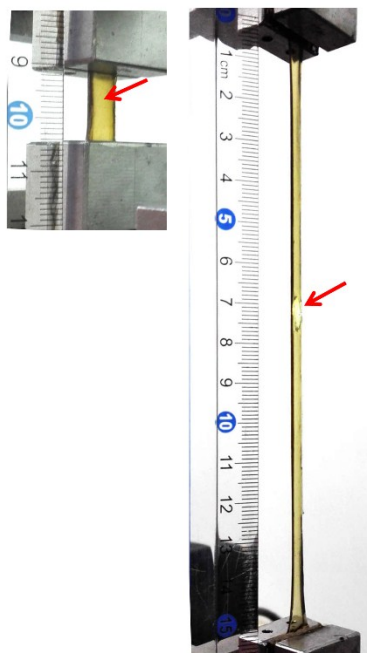


Figure S8. The tensile testing of the hydrogel with dopa: Fe^{3+} molar ratio of 1:0.8 after self-healing.

Table S1. The self-healing efficiency of hydrogel with dopa: Fe^{3+} molar ratio of 1:0.8 at different pH values after the cut samples contact for 24 hours. The values are mean values of at least 3 tests.

pH values	Elongation at break		Self-healing efficiency
	Before cutting	After self-healing	
pH=3	1575%	1340%	85.1%
pH=5	1393%	1273%	91.4%
pH=7	1041%	939%	90.2%
pH=9	1065%	1000%	93.8%
pH=11	1310%	1237%	94.5%