Light and Ferric Ion Responsive Fluorochromic Hydrogels with High Strength and Self-healing Ability

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Experimental Section

Synthesis of α-CD-SP

α-CD-SP was synthesized by esterification of SPCOOH and α-CD[1, 2]. SPCOOH (200 mg, 0.53 mmol) was was dissolved in anhydrous DMF (15 mL) in the presence of DCC (109.4 mg, 0.53 mmol) and DMAP (6.5 mg, 0.053 mmol). The solution was incubated at room temperature for 30 minutes and then α-CD (250 mg, 0.26 mmol) was added and stirred at room temperature for 24 h. After that, the solvent was removed under reduced pressure, and the solid residue was washed with acetone and then ethanol, and dried under vacuum (50% yield). The product was characterized by

^{1}H NMR, ^{13}C NMR, and HRMS (**Figure S2, S5 and S6, ESI†**). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.24-8.17 (m, 1H), 8.04-7.97 (m, 1H), 7.15 (m, 3H), 6.89-6.76 (m, 2H), 6.64 (m, 1H), 5.98 (dd, J = 10.4, 2.6 Hz, 1H), 5.64-5.34 (m, 12H), 4.78 (d, J = 3 Hz, 6H), 4.48 (t, J = 5.7 Hz, 5H), 3.94-3.54 (m, 24H), 3.52-3.45 (m, 2H), 3.45-3.37 (m, 6H), 3.29-3.24 (m, 6H), 2.71-2.53 (m, 2H), 1.17 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 171.3, 159.1, 156.7, 153.3, 146.1, 140.6, 135.7, 128.2, 127.7, 125.7, 122.8, 121.8, 119.4, 118.9, 115.5, 106.6, 101.9 (C1 of α-CD), 82.1 (C4 of α-CD), 73.3 (C5 of α-CD), 72.1 (C2 and C3 of α-CD), 60.0 (C6 of α-CD), 52.5, 33.4, 25.3, 24.5, 19.5. HRMS (ESI) m/z calcd. for $C_{57}H_{79}N_2O_{34}$ $(M+H)^+$ 1335.4509, found 1335.4506. It was estimated that one spiropyran molecule was attached to per α-CD molecule by ^{1}H NMR and HRMS.

Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra were acquired by Bruker Avance Ⅲ HD 400 MHz spectrometer at room temperature with 10 mg (30 mg for ^{13}C NMR spectra) simple dissolved in 600 μL deuterated solvents. Solvent peaks in ^{1}H NMR spectra were referenced to δH 2.5 ppm for DMSO-d_6, and in ^{13}C NMR spectra was referenced to δC 39.5 ppm for DMSO-d_6.

High resolution mass spectroscopy (HRMS)

HRMS (ESI) were obtained using positive or negative ionization mode by Thermo Scientific™ Orbitrap Fusion™ Tribrid™ mass spectrometer.

Porosity measurement

The solvent replacement method was used to measure the porosity of the hydrogels. Dried hydrogel was immersed in cyclohexane overnight and weighed after excess

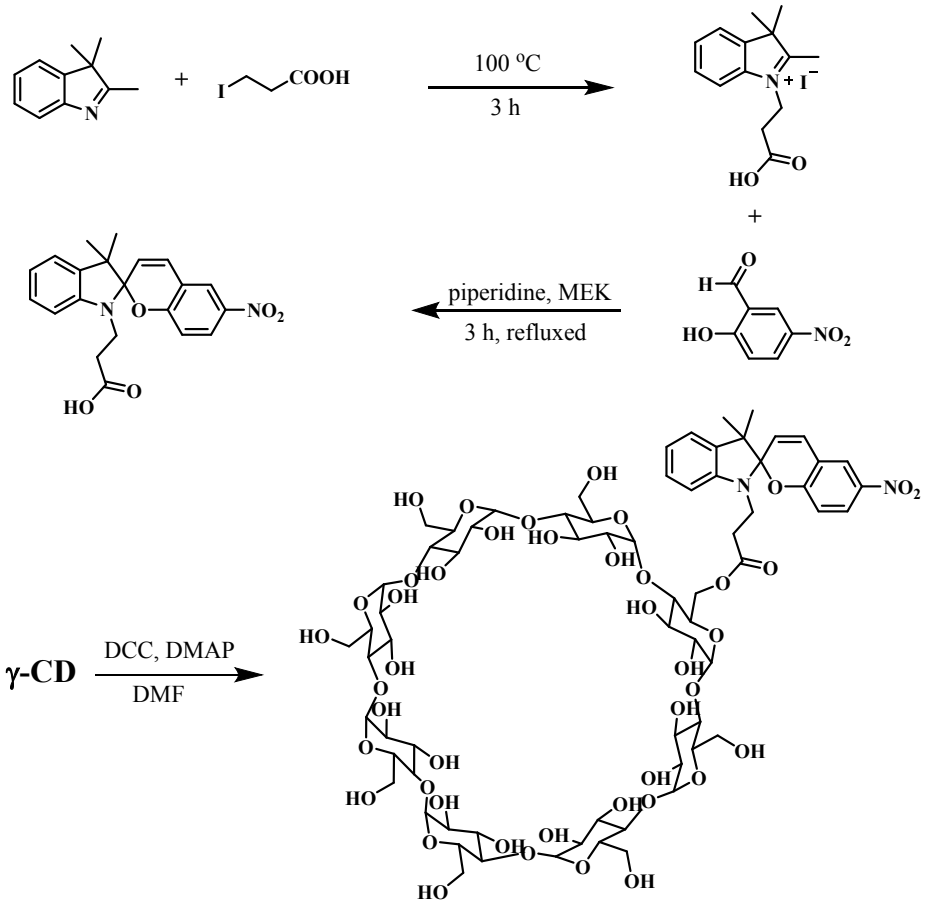
cyclohexane on the surface was blotted. The porosity was calculated from the following equation:

$$\text{Porosity}=(m_{wet}-m_{dry})/(m_1-m_2+m_{wet})$$

where m_{dry} and m_{wet} was the mass of the hydrogel before and after immersion in cyclohexane, respectively; m_1 was the mass of pycnometer with full of cyclohexane; m_2 was the mass of pycnometer contain hydrogel with full of cyclohexane. Triplicate samples were measured and the result was presented as mean ± SD.

Fourier transform infrared spectroscopy (FT-IR)

Infrared spectrometry (NICOLET iS50 FT-IR, Thermo Fisher Scientific, USA) was employed to characterize the PVA film containing TA, PVA film containing TA and Fe^{3+}, PVA film containing TA, Fe^{3+}, and EDTA. The films were prepared by solution casting method. Briefly, 200 μL of 1% PVA in aqueous solution containing different component was added on the surface of glass, and dried at 50 ^{o}C for 6 h to remove the water. After that, the samples were examined by infrared spectrometry and the data were collected from 400 to 4000 cm^{-1}.



Scheme S1. Synthetic route of γ-CD-SP

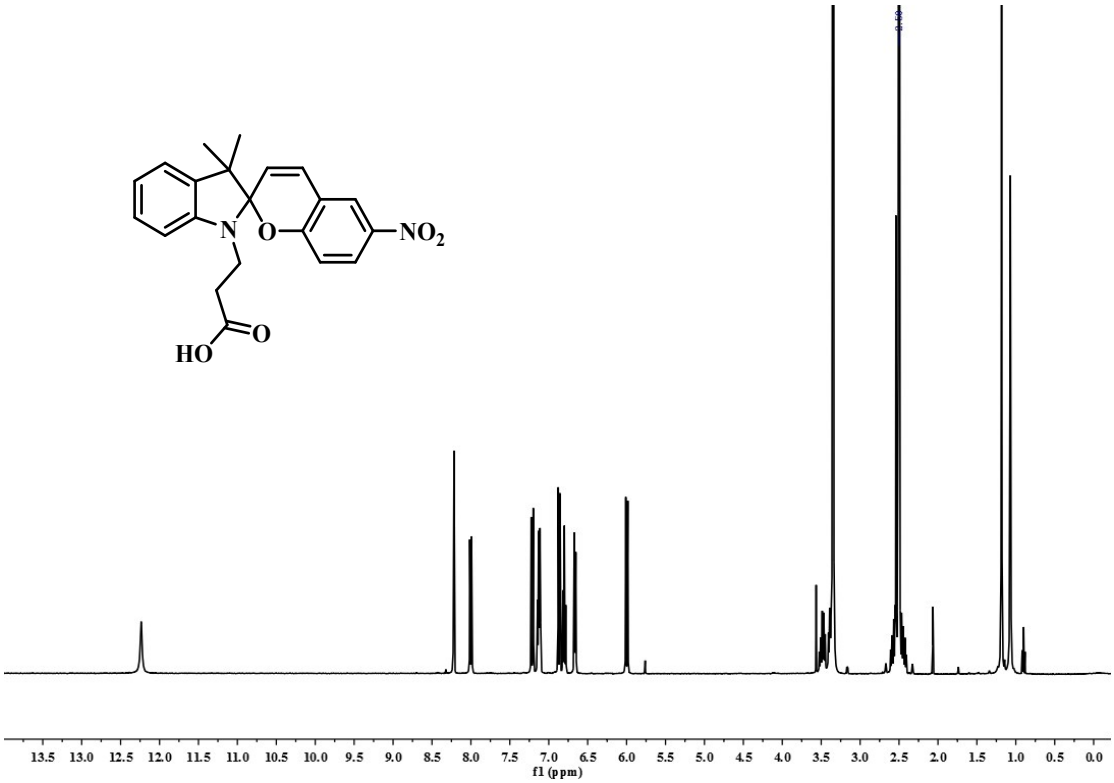


Figure S1. ^{1}H NMR spectrum of SPCOOH (DMSO-d_6)

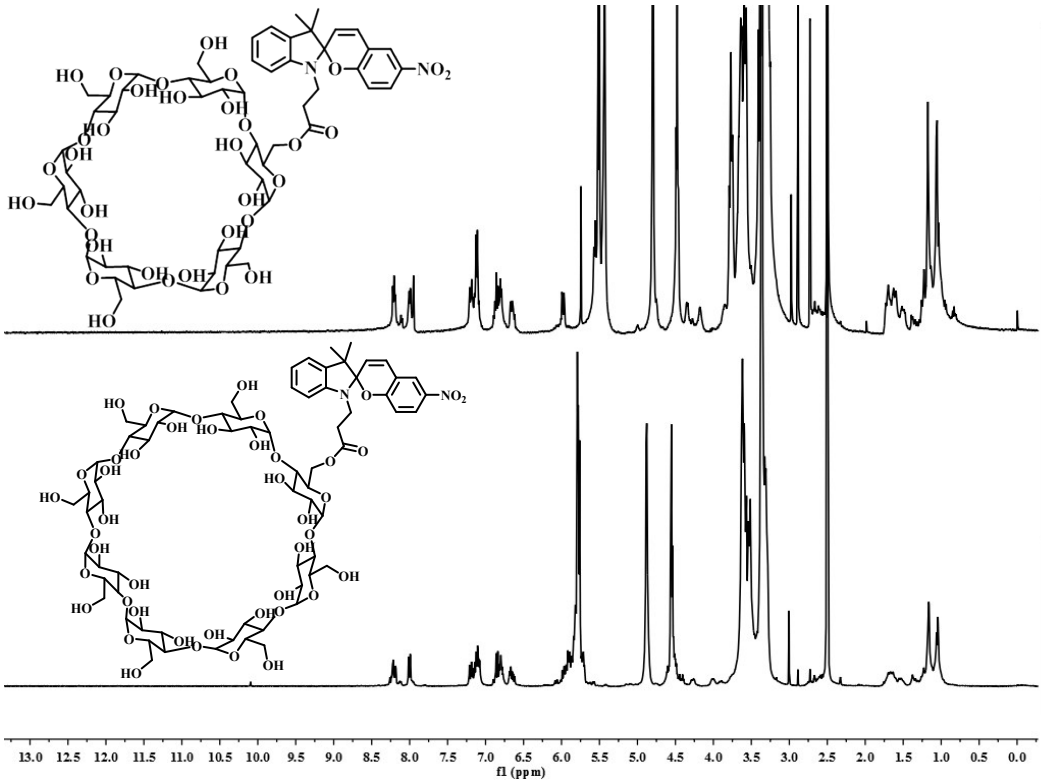


Figure S2. ^{1}H NMR of α-CD-SP and γ-CD-SP (DMSO-d_6)

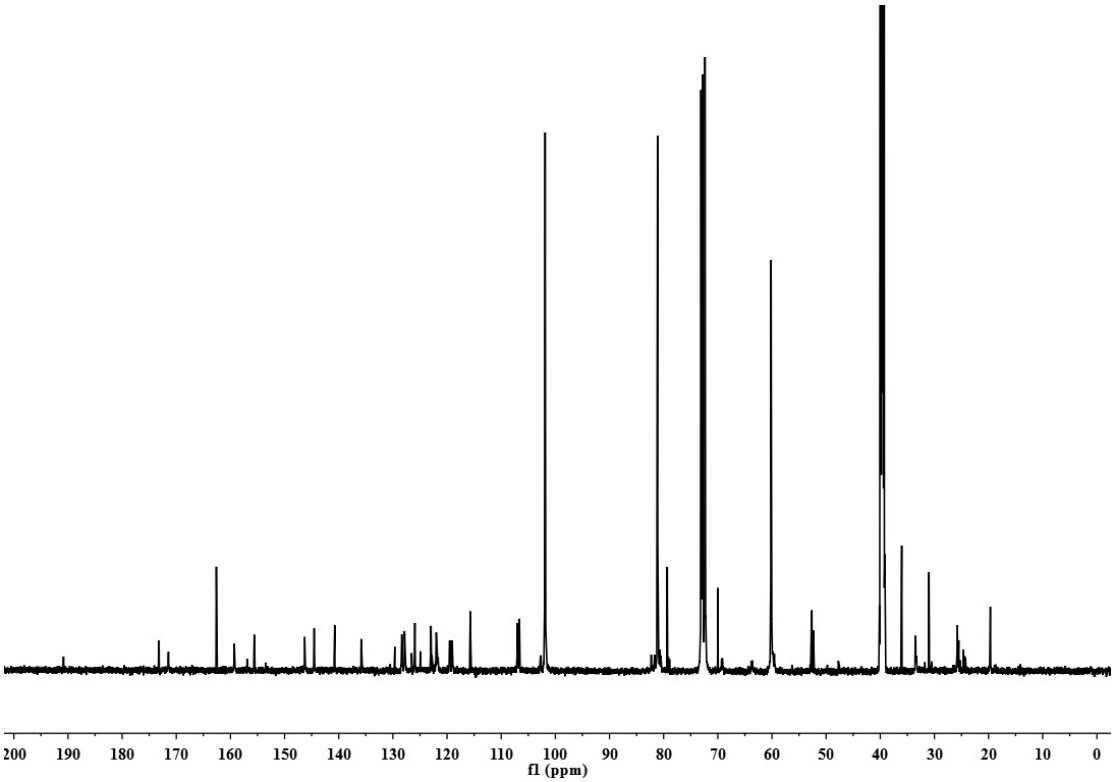


Figure S3. ^{13}C NMR of γ-CD-SP (DMSO-d_6)

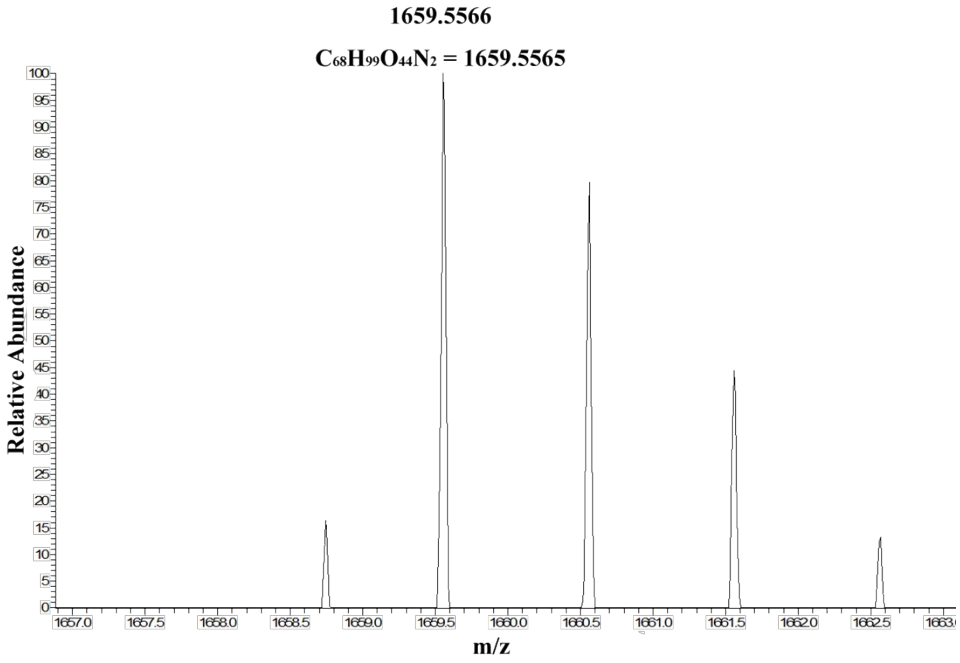


Figure S4. Mass spectrum of γ-CD-SP

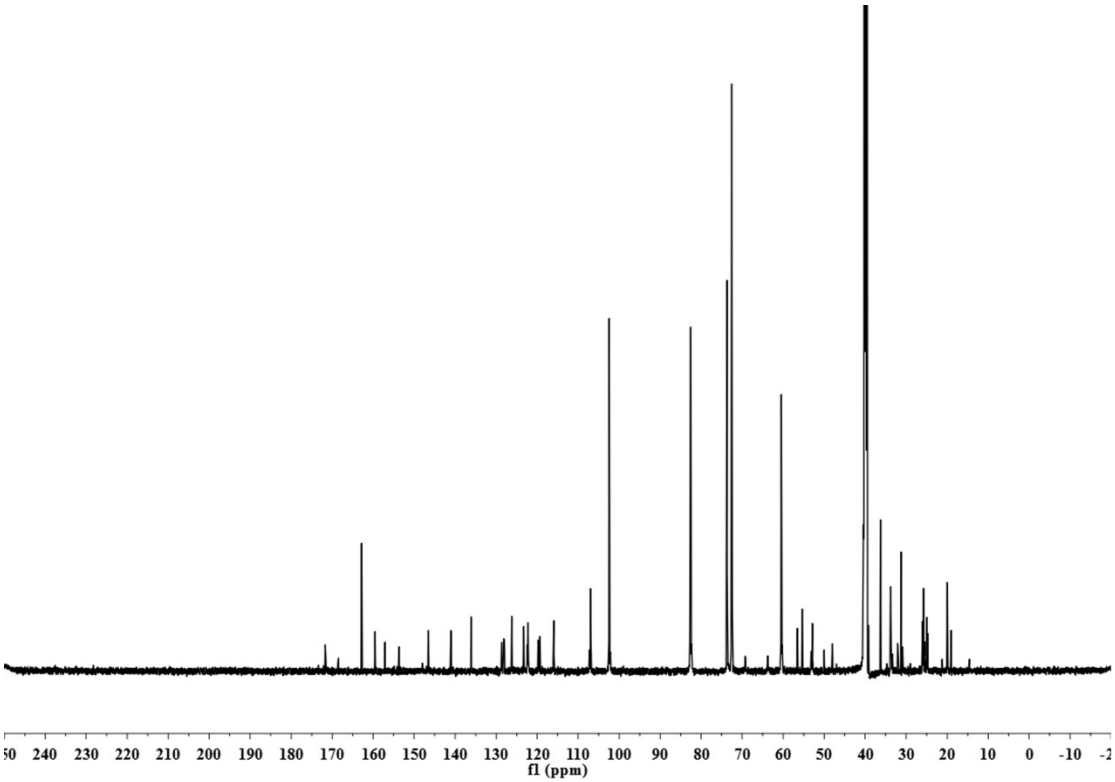


Figure S5. ^{13}C NMR spectrum of α-CD-SP (DMSO-d_6)

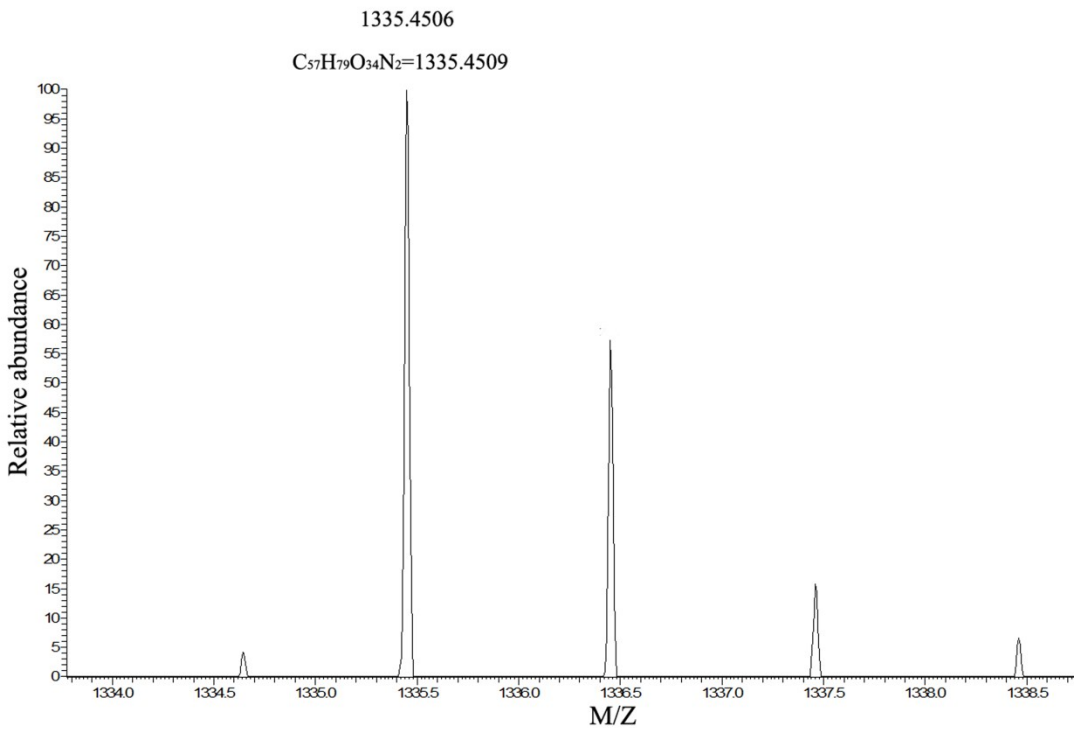


Figure S6. Mass spectrum of α-CD-SP

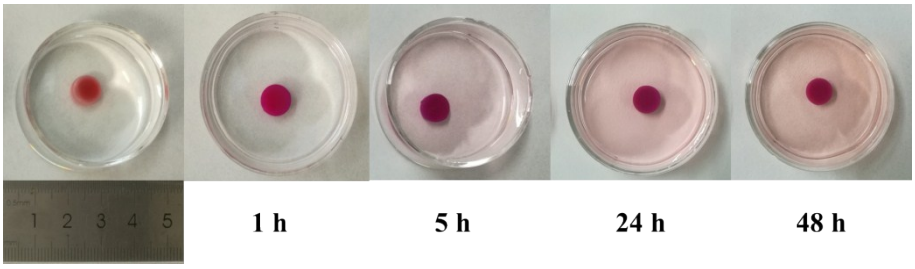


Figure S7. The photos of the PVA/α-CD-SP organogels immersed in deionized water after predetermined time.

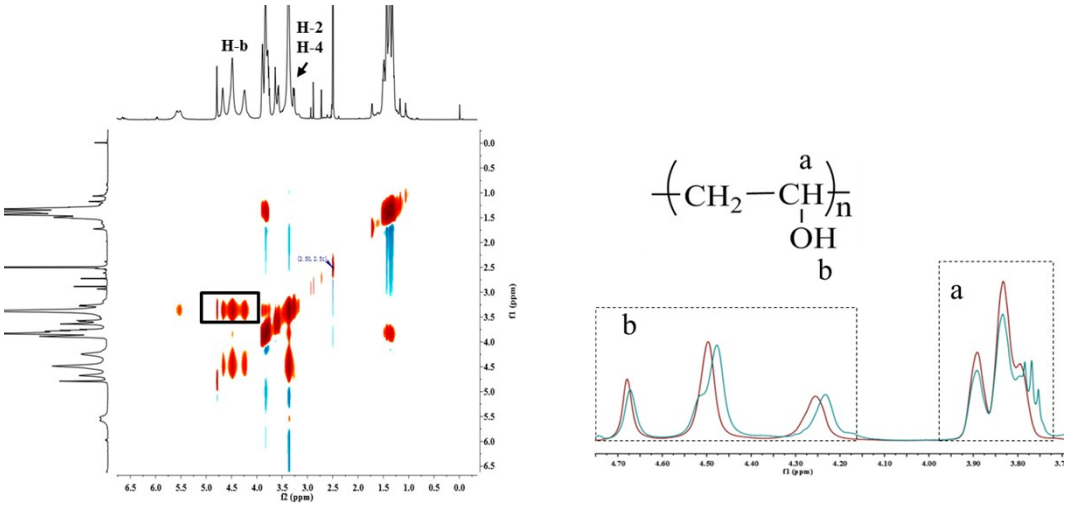


Figure S8. ^{1}H-^{1}H NOESY spectrum of PVA and α-CD-SP and the chemical shift of PVA mixed with (blue) and without (red) α-CD-SP.

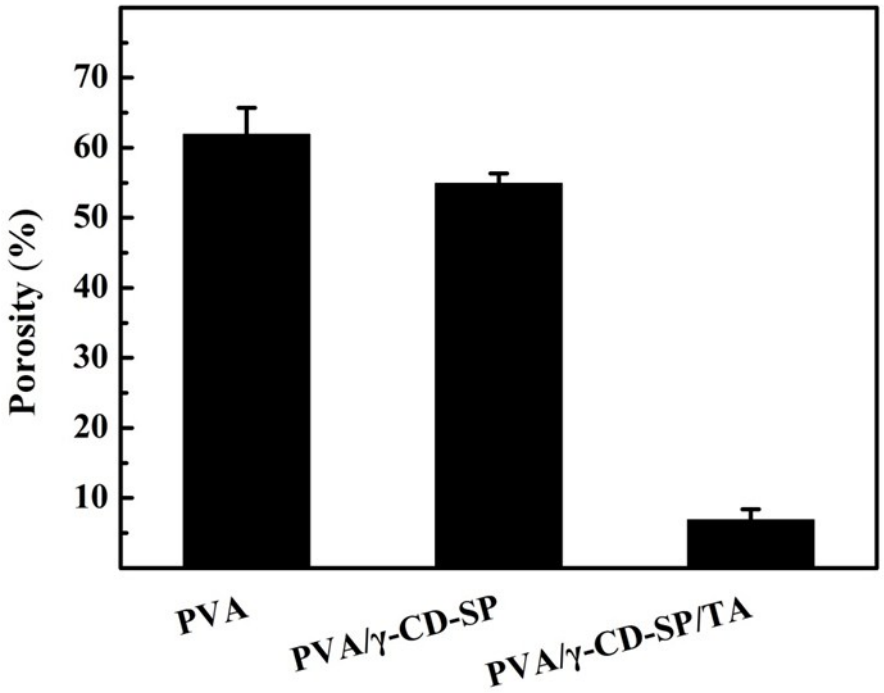


Figure S9. The porosities of the PVA, PVA/γ-CD-SP, and PVA/γ-CD-SP/TA hydrogel.

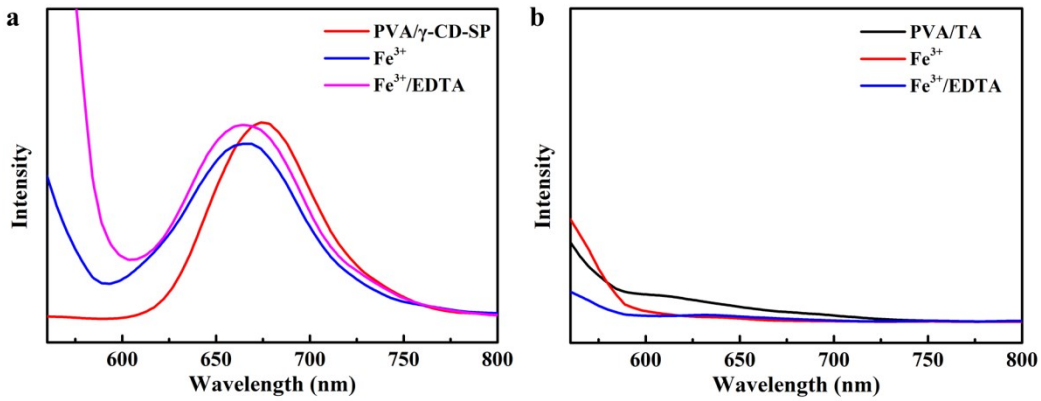


Figure S10. Fluorescence emission spectra of (a) PVA/γ-CD-SP hydrogel and (b) PVA/TA hydrogel.

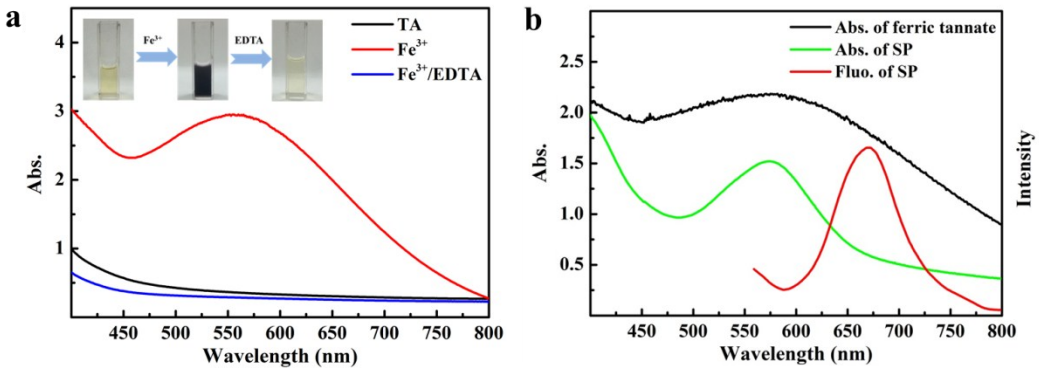


Figure S11. (a) UV-Vis absorption spectra of the TA solution with $FeCl_3$ solution and EDTA solution was added to in order; (b) UV-Vis absorption spectra of PVA/TA hydrogel treated with $FeCl_3$ solution (black line). UV-Vis absorption spectra (green line) and fluorescence emission spectra (red line) of PVA/γ-CD-SP hydrogel.

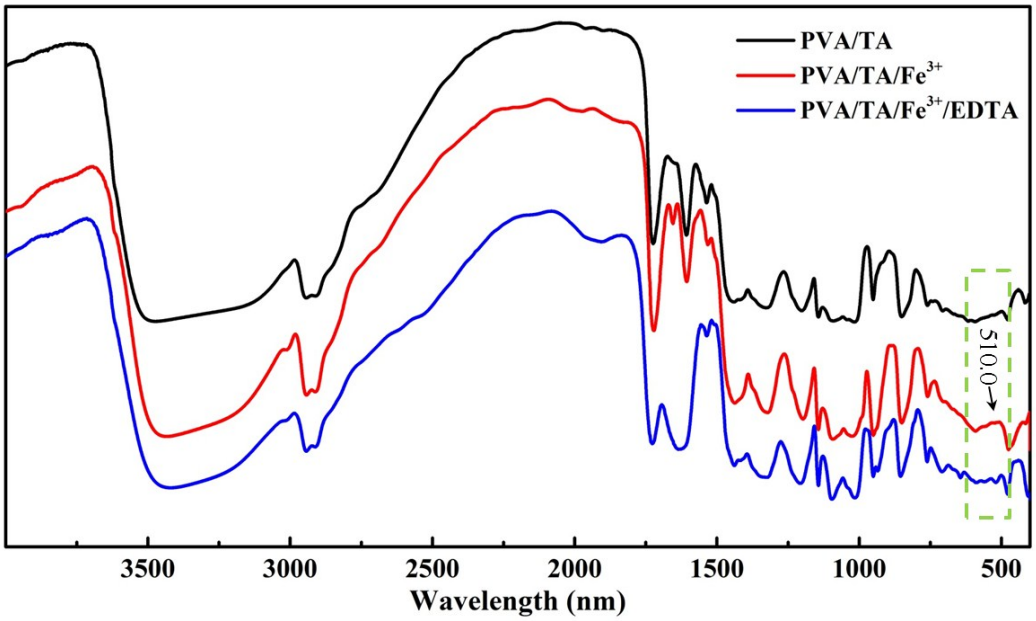


Figure S12. FT-IR spectra of PVA film containing TA, TA/Fe^{3+}, and TA/Fe^{3+}/ EDTA.

1. S. Z. Wu, Y. L. Luo, F. Zeng, J. Chen, Y. N. Chen and Z. Tong, *Angew Chem*, 2007, **46**, 7015-7018.

2. F. B. De Sousa, J. D. T. Guerreiro, M. L. Ma, D. G. Anderson, C. L. Drum, R. D. Sinisterra and R. Langer, *J Mater Chem*, 2010, **20**, 9910-9917.