



Supporting Information

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A Reversibly Responsive Fluorochromic Hydrogel Based on Lanthanide–Mannose Complex

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Supporting Information

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Experimental Section

Fourier transform infrared spectra (FTIR). FTIR spectra were collected on a Bruker TENSOR27

spectrometer. The dry samples were grinded with spectroscopic grade potassium bromide and then compressed into disks.

Inductively coupled plasma mass spectrometry (ICP). First, 800 μ L hydrogel was soaked with 200 μ L Fe²⁺ solution (10^{-3} M) for 30 min, then the supernatant was sucked out as sample 1; second, the hydrogel was soaked with 200 μ L EDTA solution (10^{-4} M) for 30 min, then the supernatant was sucked out as sample 2. The iron content in the supernatant sample 1&2 was quantified by Thermo iCAP 7400 ICP-OES.

Cytotoxicity assays. Smooth muscle cells (SMCs) were seeded into wells of cell culture plate and incubated at 37 °C in CO₂ incubator overnight. First, 10 μ L/well leach liquor of Ln-Man-Geln hydrogels was added and was incubated with cells for 24 h. Next, 10 μ L 3-(4,5-Dimethylthiazol-2-yl)-2,5-Diphenyltetrazolium Bromide (MTT) solution and 90 μ L fresh medium was added to each well, and cultured for another 4 h. Then, the supernatant was removed and 100 μ L Formazan solvent was added to each well. After the crystals being dissolved, the absorbance at 490 nm was tested by a BioTek Synergy/H1 microplate reader.

Figures and Captions

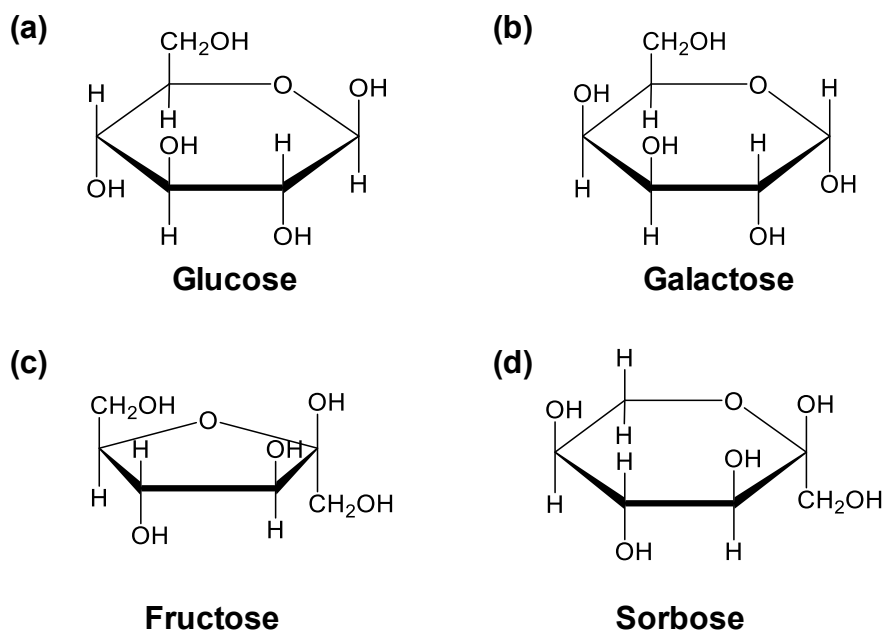


Figure S1. The structure of saccharides: (a) glucose, (b) galactose, (c) fructose, and (d) sorbose.

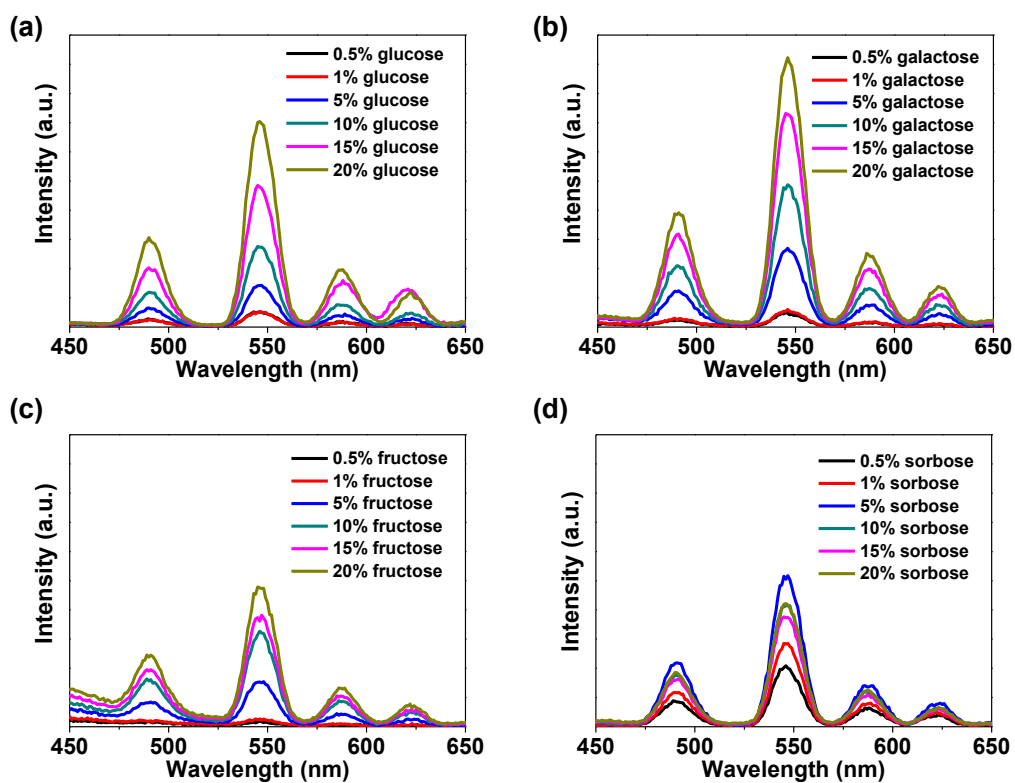


Figure S2. Fluorescent emission spectra of Tb^{3+} -saccharides complexes with different concentration of saccharides upon 312 nm excitation: (a) Tb^{3+} -glucose complex, (b) Tb^{3+} -galactose complex, (c) Tb^{3+} -fructose complex, and (d) Tb^{3+} -sorbose complex.

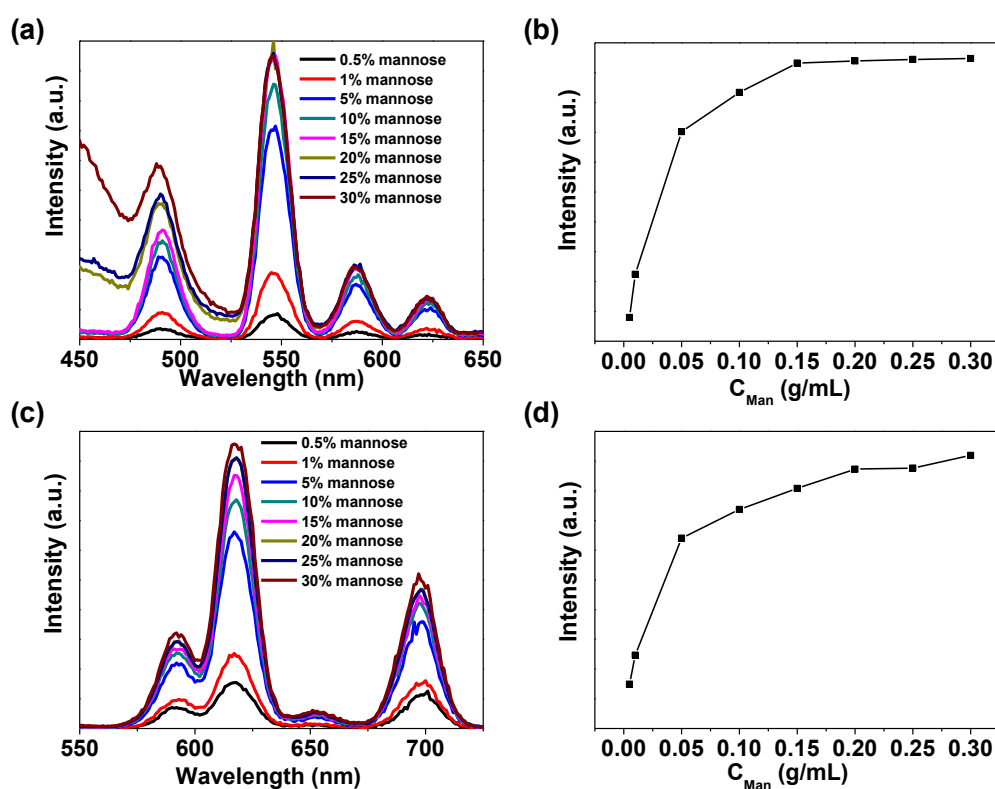


Figure S3. (a) Fluorescent emission spectra of Tb-Man complexes with different concentration of mannose upon 312 nm excitation. **(b)** Fluorescence intensity of Tb-Man complexes at 545 nm. **(c)** Fluorescent emission spectra of Eu-Man complexes with different concentration of mannose upon 312 nm excitation. **(d)** Fluorescence intensity of Eu-Man complexes at 615 nm.

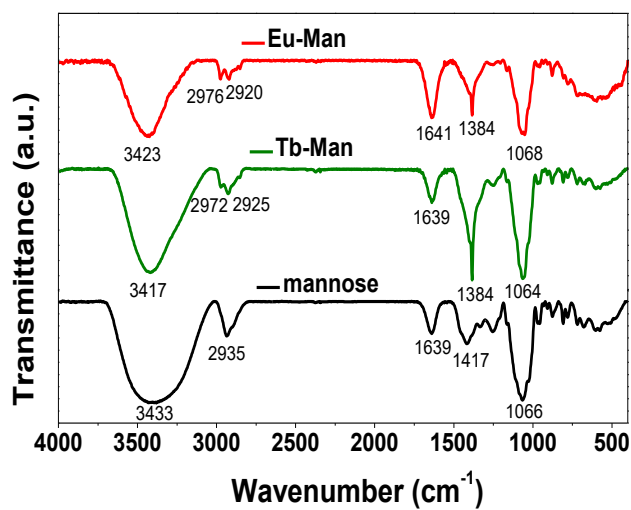


Figure S4. FT-IR spectra of mannose, Tb-Man complex and Eu-Man complex.

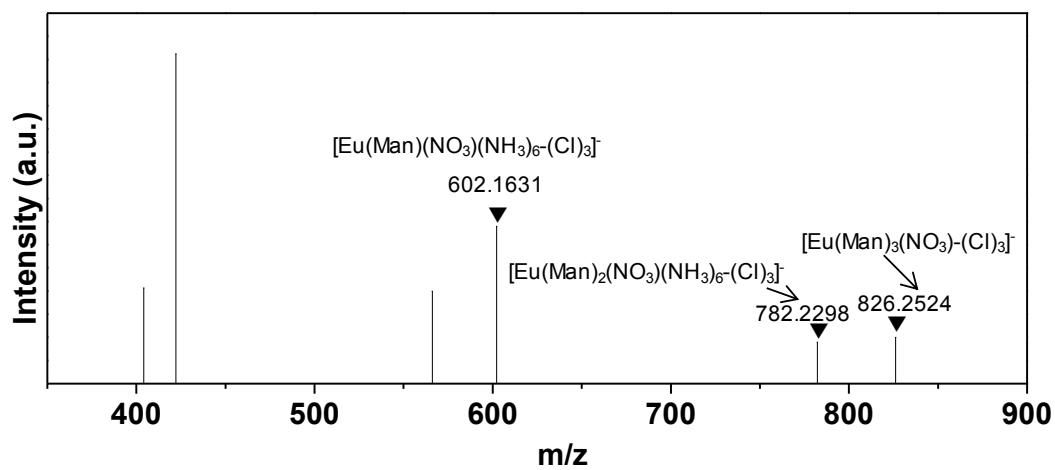


Figure S5. MALDI-MS spectrum of Eu-Man complex.

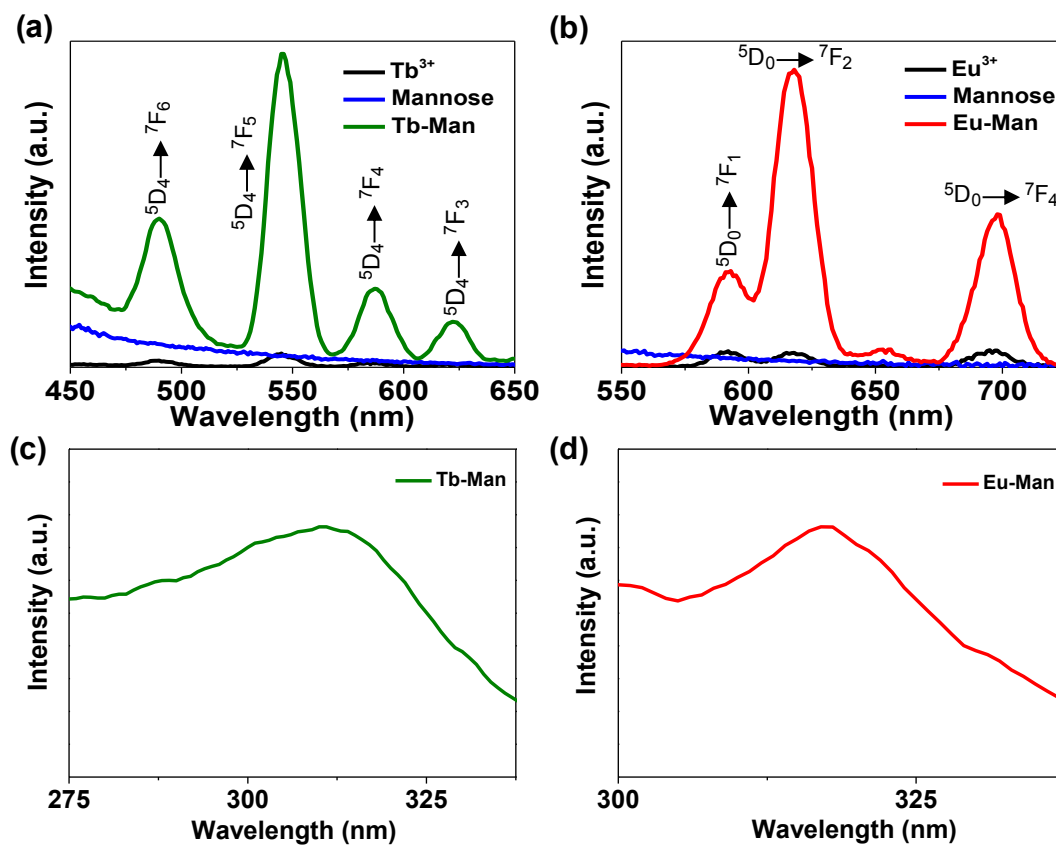


Figure S6. (a&b) Fluorescent emission spectra of Tb^{3+} , mannose and Tb-Man complex (a) and Eu^{3+} , mannose and Eu-Man complex (b). (c&d) Fluorescent excitation spectra of Tb-Man complex (c) and Eu-Man complex (d).

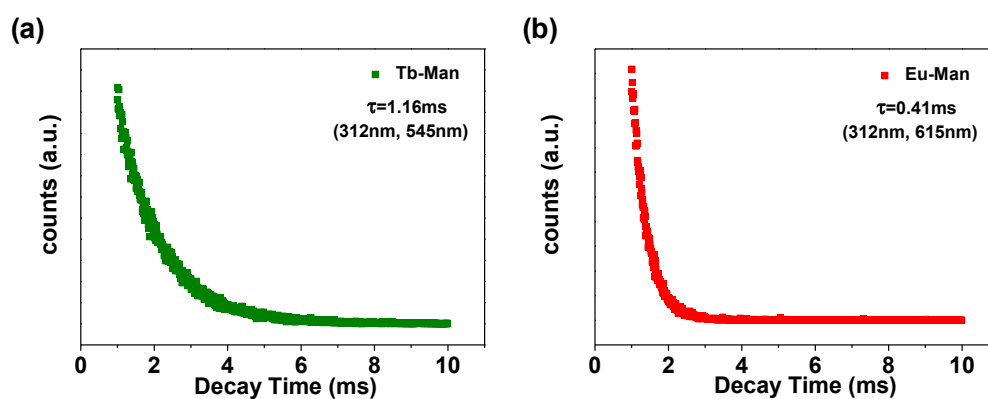


Figure S7. (a&b) The decay curves of Tb-Man complex (a) and Eu-Man complex (b).

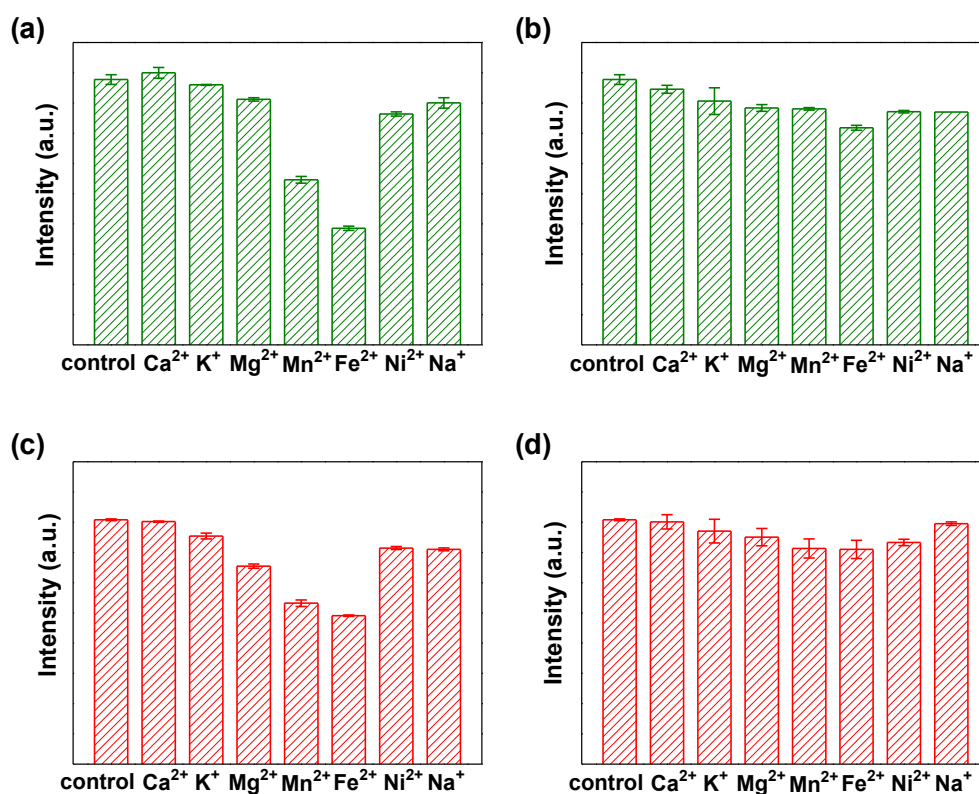


Figure S8. Fluorochromic responses of Tb-Man complex and Eu-Man complex upon metal ions with varied concentration: **(a&c)** 2×10^{-4} M, **(c&d)** 2×10^{-5} M.

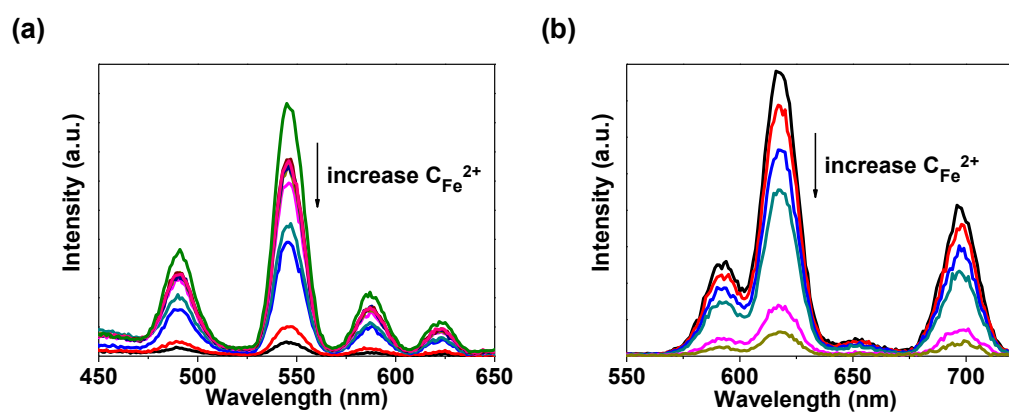


Figure S9. **(a&b)** Gradual decrease in the fluorescence intensity of Tb-Man complex (a) and Eu-Man complex (b) by increasing the concentration of Fe²⁺ ion.

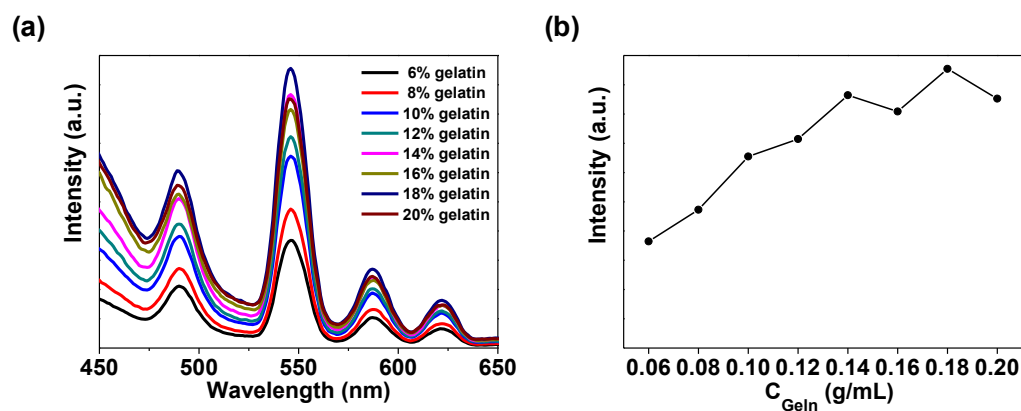


Figure S10. (a) Fluorescent emission spectra of Tb-Man-GelN hydrogel with different concentration of gelatin upon 312 nm excitation. (b) Fluorescence intensity of Tb-Man-GelN hydrogel at 545 nm.

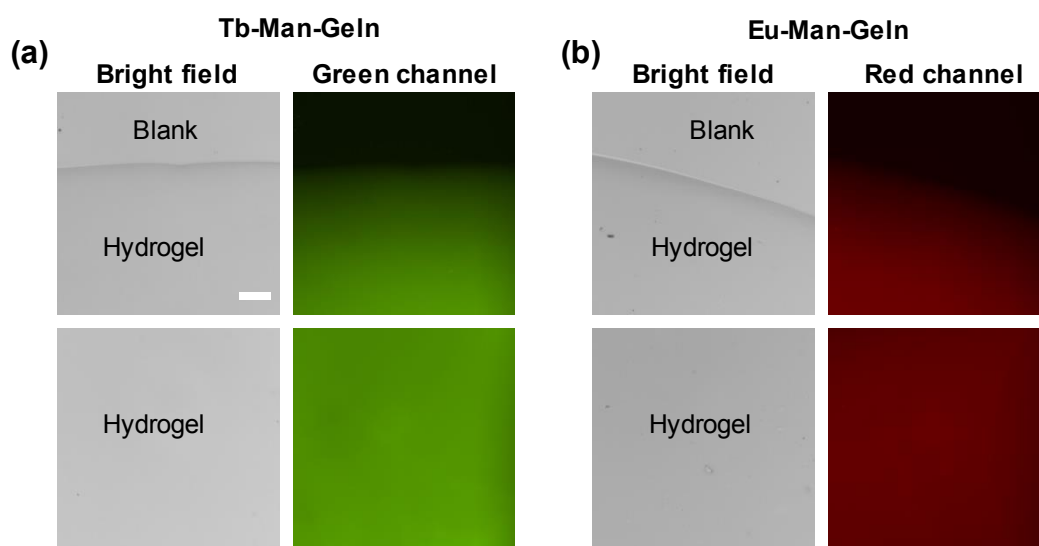


Figure S11. (a&b) Fluorescence microscopy images of Tb-Man-GelN hydrogel (a) and Eu-Man-GelN hydrogel (b). Scale bar represents 60 μm .

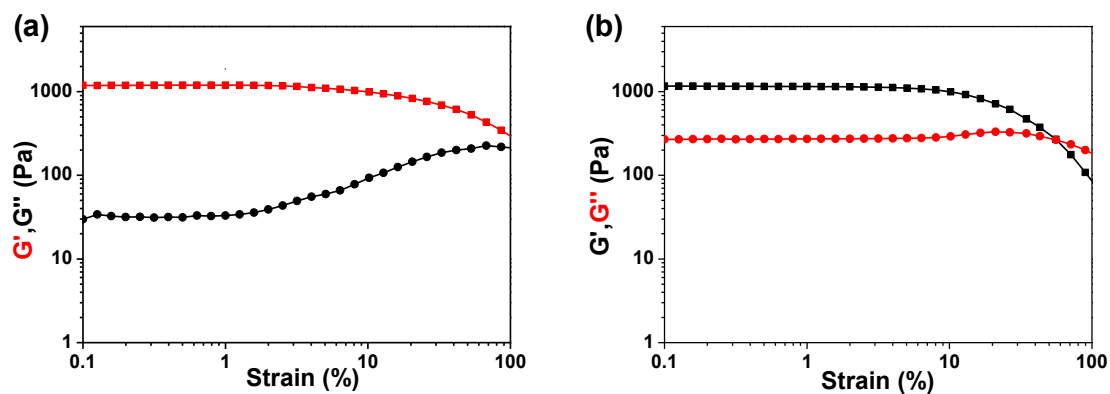


Figure S12. The rheology properties of gelatin (a) and Eu-Man-Geln hydrogel (b).

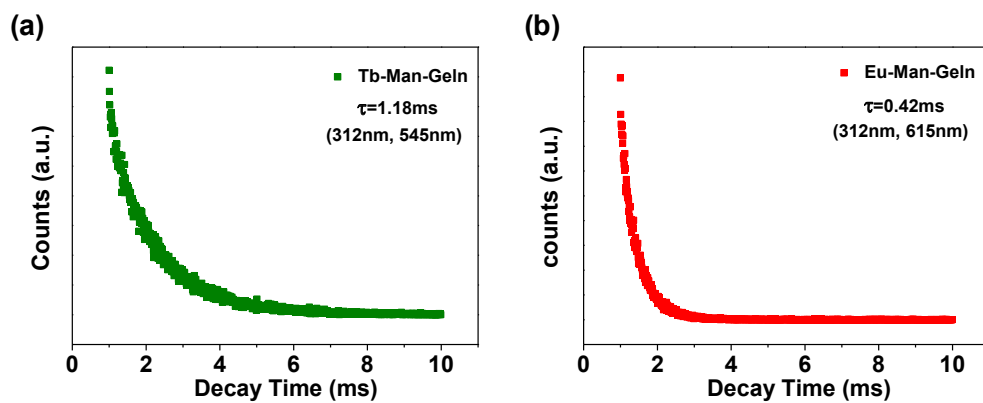


Figure S13. (a&b) The decay curves of Tb-Man-Geln hydrogel (a) and Eu-Man-Geln hydrogel (b).

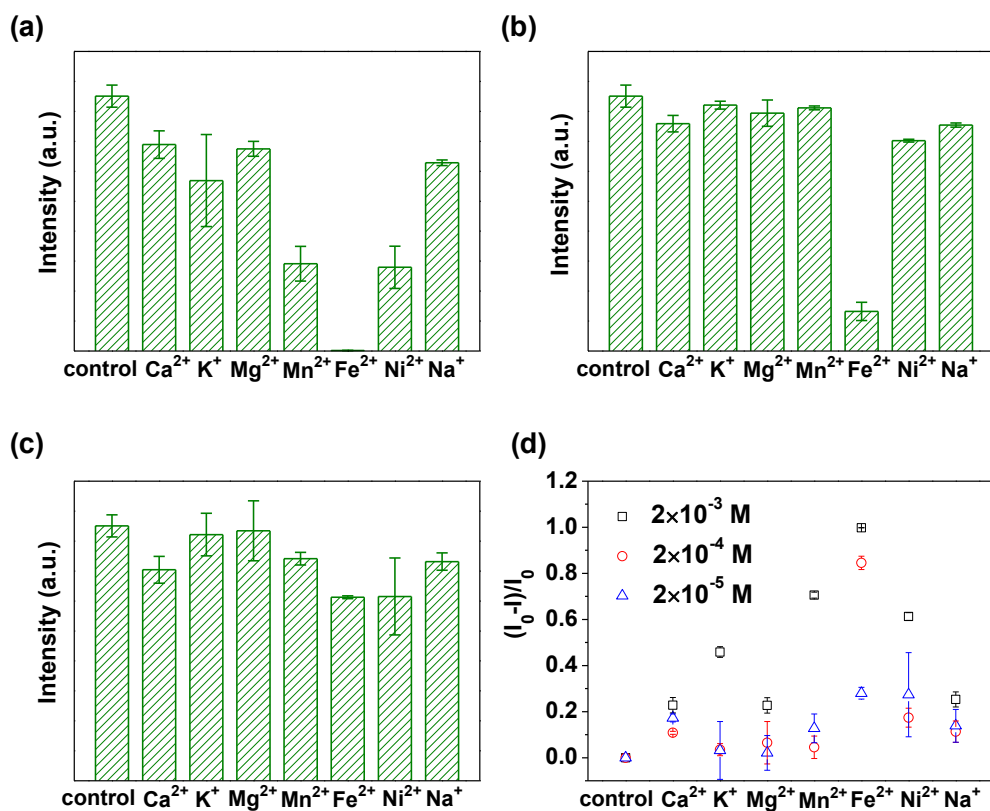


Figure S14. Fluorochromic responses of Tb-Man-Geln hydrogel upon metal ions with varied concentration: **(a)** 2×10^{-3} M, **(b)** 2×10^{-4} M, **(c)** 2×10^{-5} M, **(d)** The quenching efficiency upon metal ions with varied concentration.

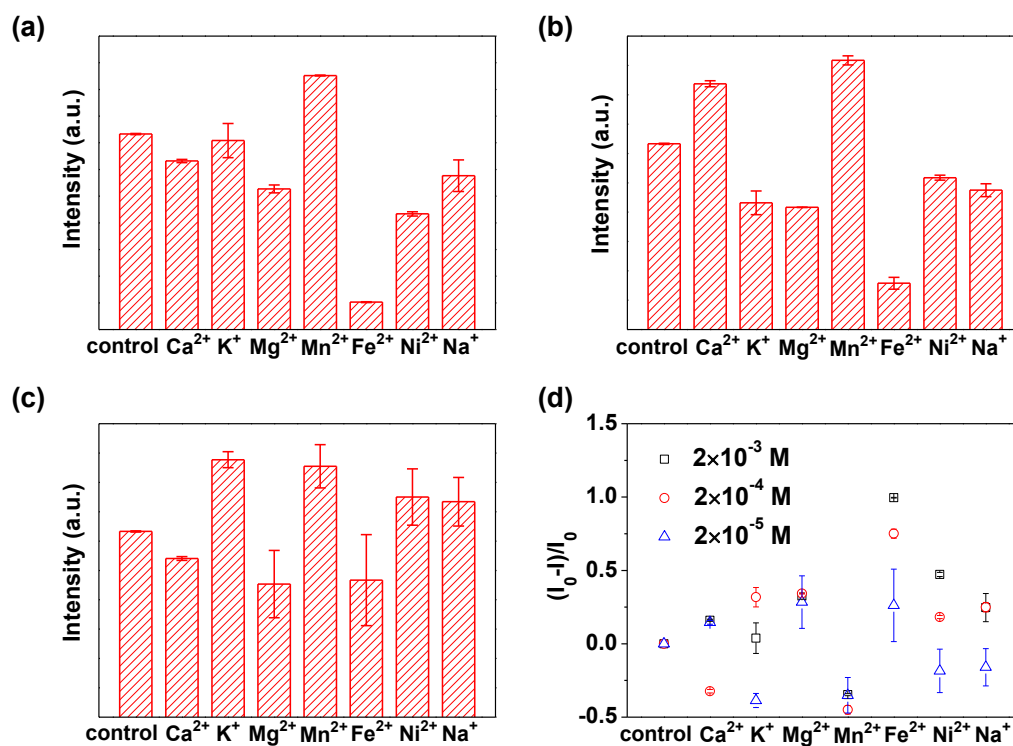


Figure S15. Fluorochromic responses of Eu-Man-Geln hydrogel upon metal ions with varied concentration: (a) 2×10^{-3} M, (b) 2×10^{-4} M, (c) 2×10^{-5} M, (d) The quenching efficiency upon metal ions with varied concentration.

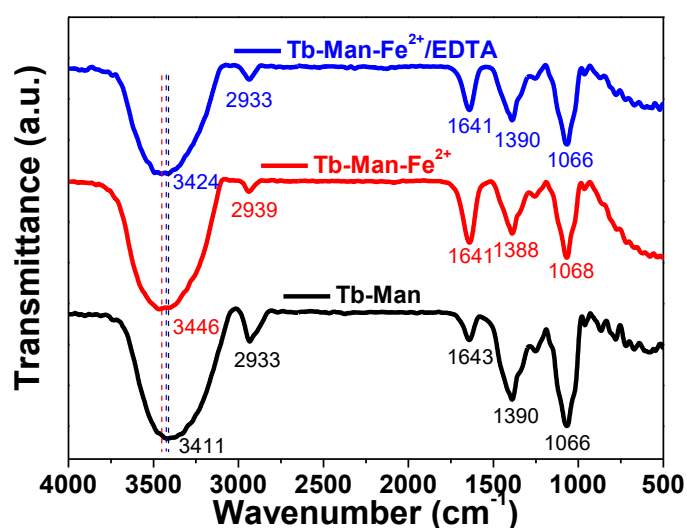


Figure S16. FTIR spectra of Tb-Man complex, upon the addition of Fe²⁺ and upon the addition of EDTA.

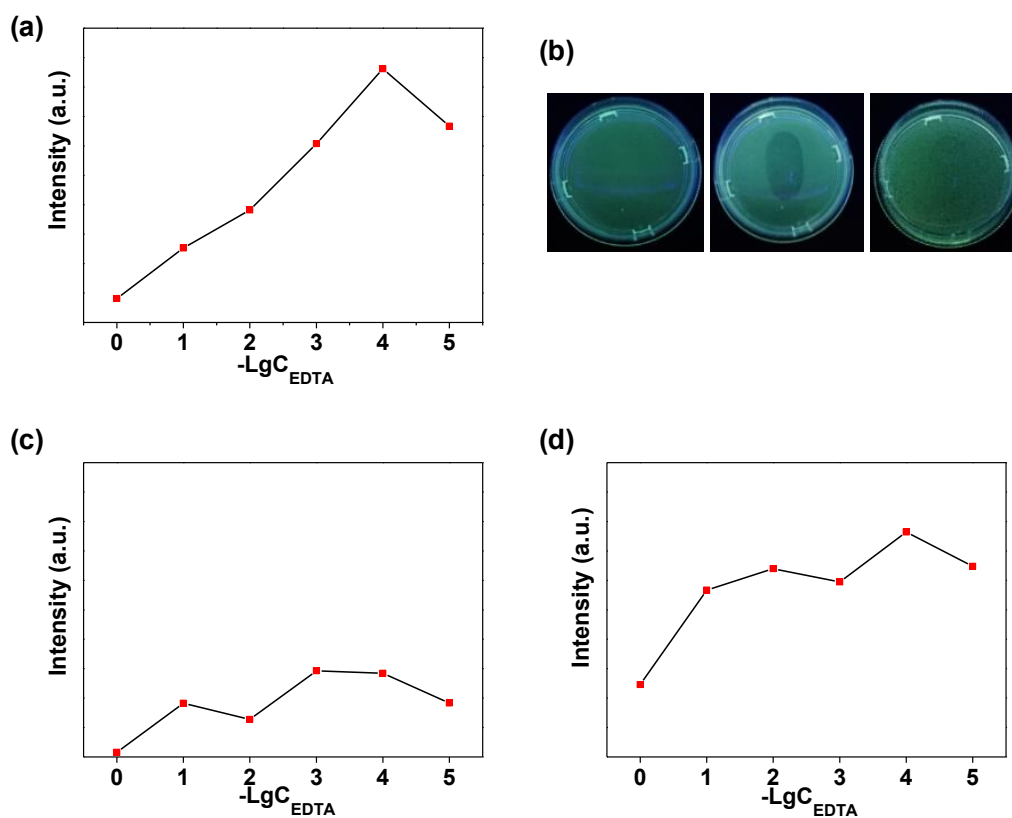


Figure S17. (a) The recovered Tb-Man-GelN hydrogel by adding different concentration of EDTA upon adding Fe^{2+} with final concentration of $2 \times 10^{-4} \text{ M}$. (b) The photographs of Tb-Man-GelN hydrogel in a Petri dish under 312 nm UV light: the fluorescence of original hydrogel (left); the fluorescence of hydrogel quenched by pressing fingerprint with Fe^{2+} ion (middle); and the fluorescence of hydrogel recovered by adding EDTA (right). (c&d) The recovered Eu-Man-GelN hydrogel by adding varied concentration of EDTA upon adding different final concentration of Fe^{2+} : $2 \times 10^{-3} \text{ M}$ (c), $2 \times 10^{-4} \text{ M}$ (d).