

Supplementary Materials:

Optical Detection of Fe³⁺ Ions in Aqueous Solution with High Selectivity and Sensitivity by Using Sulfasalazine Functionalized Microgels

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Additional Experimental Section

1. Materials

Gadolinium(III) nitrate hexahydrate (Gd(NO₃)₃·6H₂O, 99.9%), lithium nitrate (LiNO₃, 99%), cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99%), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O, 97.5%), bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 98%), ytterbium(III) nitrate pentahydrate (Yb(NO₃)₃·5H₂O, 99.99%), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, 98%), and lanthanum(III) nitrate hydrate (La(NO₃)₃·H₂O, 99%), were obtained from J&K Chemical Ltd. Chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, 99%) was obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Potassium nitrate (KNO₃, 99%), silver nitrate (AgNO₃, 99.8%), sodium nitrate (NaNO₃, 99%), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98.5%), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.5%), lead(II) dinitrate (Pb(NO₃)₂, 99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%), barium nitrate (Ba(NO₃)₂, 99.5%), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%), and calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 98.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd.

2. Synthesis Procedure of Sulfasalazine Functionalized Microgels (SSZ-MGs)

For the synthesis of SSZ-MGs, NIPAm (226.4 mg, 2 mmol), VIM (27 μL, 0.3 mmol), and 1,6-dibromhexane (30 μL, 0.2 mmol) were added into deionized water (50 mL) in a 100 mL three-neck flask. The mixture was then heated to 70 °C with vigorous stirring and bubbled with N₂ for 30 min. After that, 1 mL of AIBA aqueous solution (25 mg/mL) was added to the mixture to initiate the polymerization reaction. After 1 h, 1 mL of SSZ DMF solution (78.8 mg, 0.2 mmol) was added drop wise to the reaction mixture. The reaction further proceeded at 70 °C for 24 h. After polymerization, the reaction mixture was cooled down to room temperature. The reaction mixture was first dialyzed against DMF for 2 days and then deionized water for 7 days. The dialysis tubes with MWCO of 14000 were used. During dialysis, DMF or deionized water was changed every 12 h. The obtained purified microgels were named as SSZ-MGs. The yield of SSZ-MGs was about 50.3%.

N-MGs were synthesized by the same procedure without addition of SSZ molecules.

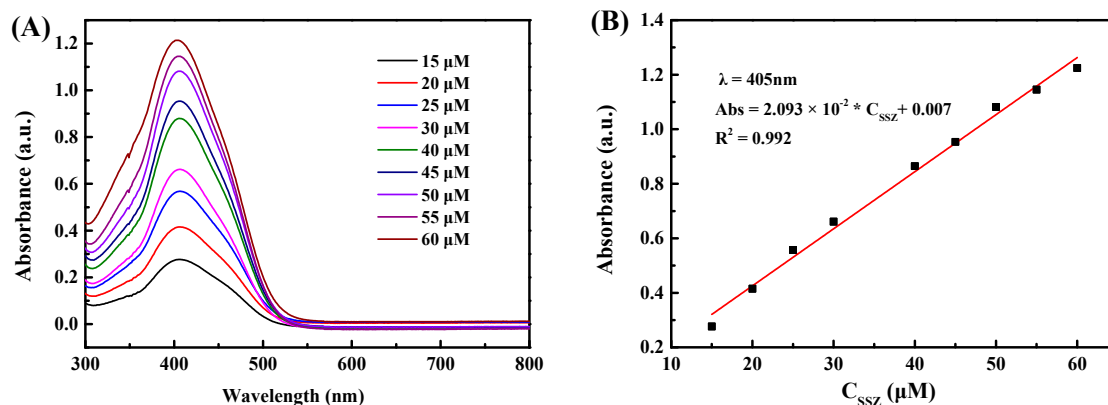


Figure S1. (A) UV-vis spectra of SSZ in DMF with various concentrations at room temperature. (B) The corresponding standard calibration curve of SSZ in DMF.

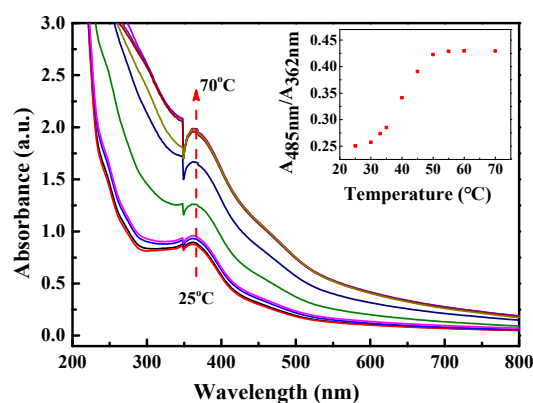
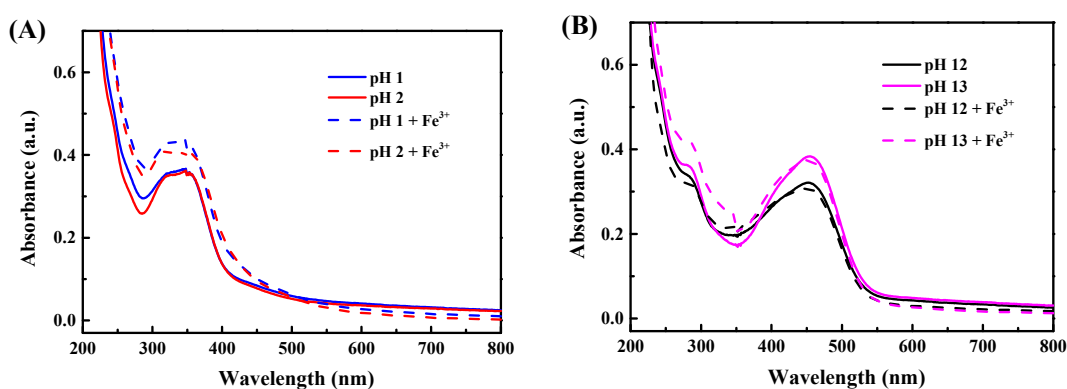


Figure S2. The UV-vis absorption spectra of SSZ-MG aqueous suspensions without the presence of Fe^{3+} ions at pH of 5.6 and various temperatures. Inset shows the corresponding $A_{485\text{nm}}/A_{362\text{nm}}$ ratios. The concentration of SSZ-MG aqueous suspensions was 0.196 mg/mL.



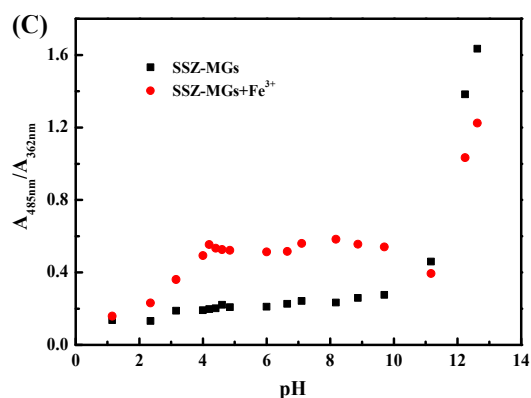


Figure S3. The UV-vis absorption spectra of SSZ-MG aqueous suspensions (0.099 mg/mL) with or without the presence of 50 μM Fe^{3+} ions at (A) pH 1 and 2, and (B) pH 12 and 13. (C) The $A_{485\text{nm}}/A_{362\text{nm}}$ ratios of SSZ-MG aqueous suspensions (0.099 mg/mL) with and without the presence of 10 μM Fe^{3+} ions at 25 $^{\circ}\text{C}$ and various pH values.

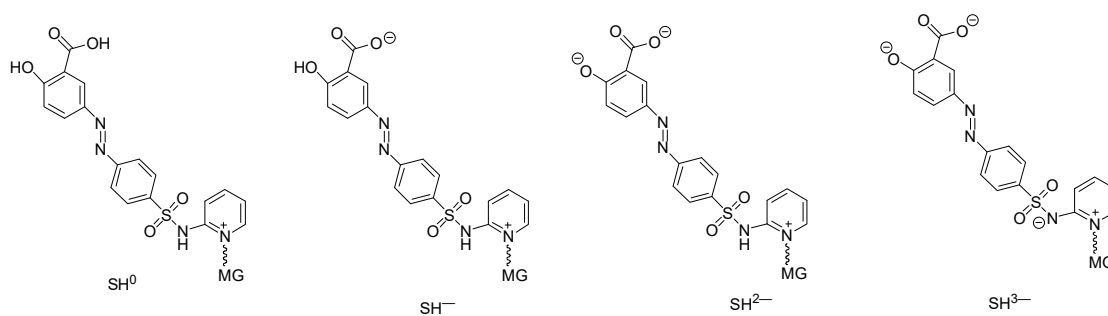


Figure S4. Possible structures of sulfasalazine (SSZ) moieties in SSZ-MG aqueous suspensions.

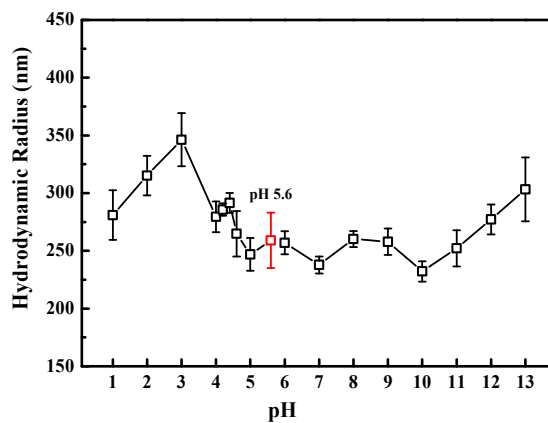


Figure S5. The hydrodynamic radius of SSZ-MG aqueous suspensions as a function of pH values at 25 $^{\circ}\text{C}$, which were adjusted by using 1 M HCl and NaOH aqueous solutions. The red circle symbol presented the hydrodynamic radius of original diluted SSZ-MG aqueous suspensions without pH adjusting.

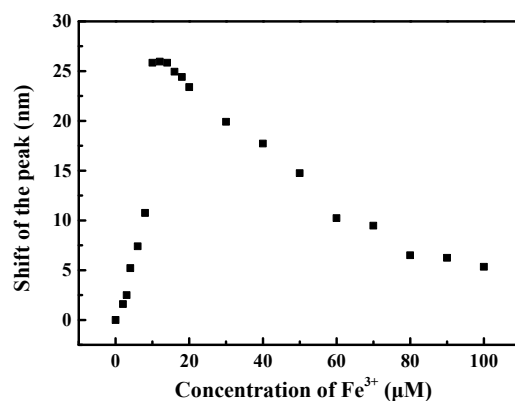


Figure S6. Wavelength shift of absorption peak at 362 nm of SSZ-MG aqueous suspensions as a function of Fe^{3+} concentration at 25 °C and pH of 5.6. The concentration of SSZ-MG aqueous suspensions was 0.174 mg/mL. The corresponding concentration of SSZ moieties ([SSZ]) in SSZ-MG aqueous suspensions was 23.09 μM .

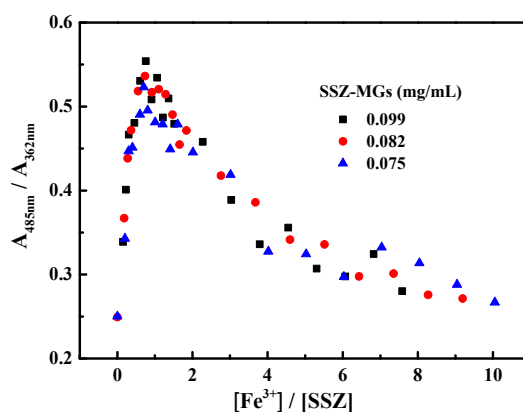


Figure S7. $A_{485\text{nm}}/A_{362\text{nm}}$ ratios as a function of $[\text{Fe}^{3+}]/[\text{SSZ}]$ for SSZ-MG aqueous suspensions with various concentrations at 25 °C and pH of 5.6. The concentrations of SSZ-MG aqueous suspensions were 0.099, 0.082, and 0.075 mg/mL, respectively. The corresponding concentrations of SSZ moieties were 13.19, 10.88, and 9.95 μM , respectively.

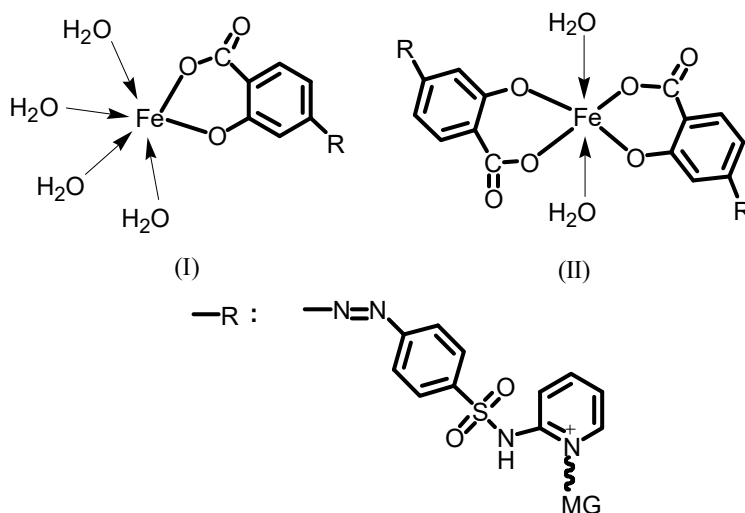


Figure S8. Possible coordination structures of SSZ moieties and Fe^{3+} ion.

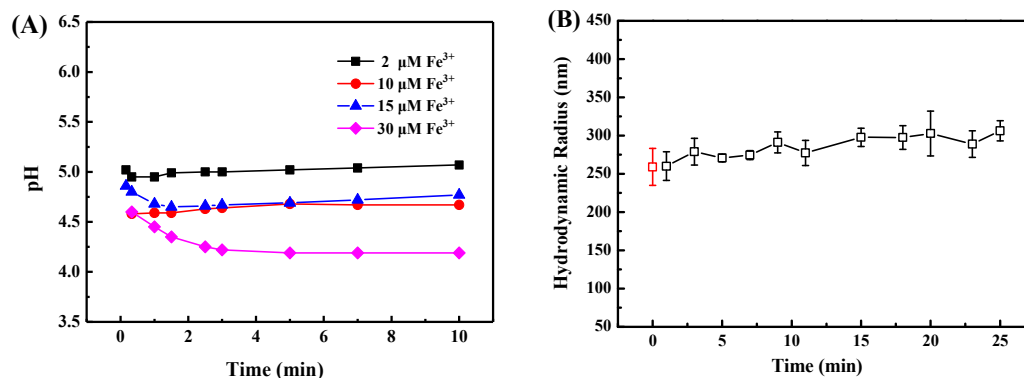


Figure S9. (A) The pH values of SSZ-MG aqueous suspensions (0.174 mg/mL) as a function of time monitored immediately after addition of 2, 10, 15, and 30 μM Fe^{3+} ions at 25 °C. (B) The hydrodynamic radius of SSZ-MG aqueous suspensions (0.174 mg/mL) as a function of time measured by DLS immediately after addition of 10 μM Fe^{3+} ions at 25 °C. The red symbol was the hydrodynamic radius of original SSZ-MG aqueous suspensions.

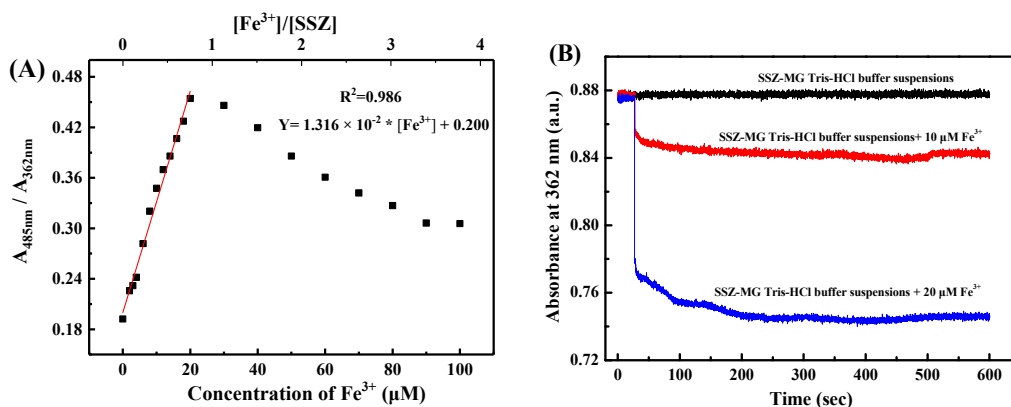


Figure S10. (A) The $A_{485\text{nm}}/A_{362\text{nm}}$ ratio of SSZ-MG Tris-HCl buffer suspensions (0.196 mg/mL) as a function of Fe^{3+} concentration ($[\text{Fe}^{3+}]$) as well as $[\text{Fe}^{3+}]/[\text{SSZ}]$ ratio. (B) Plot of absorption intensity at 362 nm of SSZ-MG Tris-HCl buffer suspensions (0.196 mg/mL) as a function of time after adding 10 and 20 μM Fe^{3+} ions.

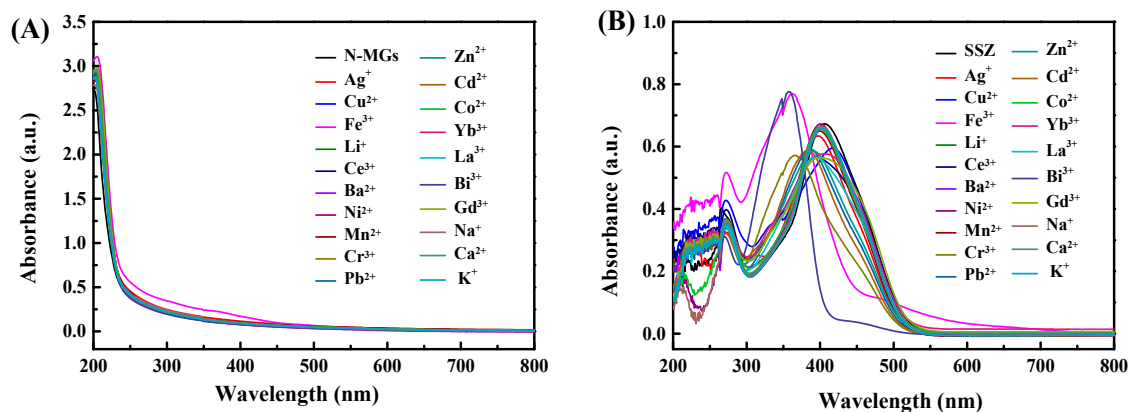


Figure S11. (A) The UV-vis absorption spectra of N-MG aqueous suspensions (0.099 mg/mL) after addition of 50 μM various metal ions, respectively, at 25 $^{\circ}\text{C}$ and pH of 5.6. (B) The UV-vis absorption spectra of SSZ molecules in DMF (0.012 mg/mL) with the presence of 50 μM various metal ions, respectively.

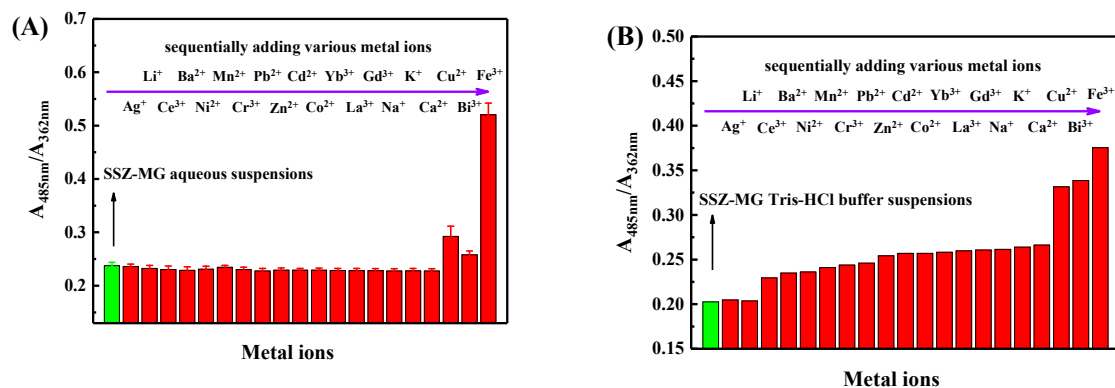


Figure S12. (A) The $A_{485\text{nm}}/A_{362\text{nm}}$ ratios of SSZ-MG aqueous suspensions (0.196 mg/mL, pH 5.6) upon sequential addition of different metal ions (10 μM) at 25 $^{\circ}\text{C}$. (B) The $A_{485\text{nm}}/A_{362\text{nm}}$ ratios of SSZ-MG Tris-HCl buffer suspensions (0.196 mg/mL, pH 7.1) upon sequential addition of different metal ions (10 μM) at 25 $^{\circ}\text{C}$. The addition sequences of metal ions were Ag^+ , Li^+ , Ce^{3+} , Ba^{3+} , Ni^{2+} , Mn^{2+} , Cr^{3+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Yb^{3+} , La^{3+} , Gd^{3+} , Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Bi^{3+} , and Fe^{3+} for (A) and (B).

Table S1. Concentrations of Fe^{3+} ions spiked in deionized water, lake water, and drinking water from Yuquan campus of Zhejiang University as determined by UV-vis absorption spectroscopy with SSZ-MG aqueous suspensions (0.082 mg/mL) as the optical sensor.

Sample	$[\text{Fe}^{3+}]$ Measured by Elemental Analysis (nM)	$[\text{Fe}^{3+}]$ spiked (μM)	$[\text{Fe}^{3+}]$ Measured by UV-Vis Spectroscopy (nM)
deionized water	0	4	3960 ± 76
		8	8079 ± 38
		10	10057 ± 59
lake water	23 ± 13	4	3938 ± 90
		8	8111 ± 41
		10	9994 ± 148
drinking water	43 ± 10	4	4100 ± 64
		8	8037 ± 133
		10	10088 ± 45