Electronic Supplementary Material (ESI) for New Journal of Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

New Journal of Chemistry

Selective Colorimetric Sensing of Deferoxamine with 4-Mercaptophenol− and Mercaptoacetic acid−Functionalized Gold Nanoparticles *via* Fe(III)-Chelation

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Table of Contents

1. Abbreviations

DFO, deferoxamine; 4MP, 4-mercaptophenol; MAA, mercaptoacetic acid; AuNPs, gold-nanoparticles; NaOH, sodium hydroxide; MeOH, methanol; FA, formic acid.

2. Preparation of Solutions

For Au-nanoparticles synthesis, $HAuCl_4$ solution (0.01%, *w*/*v*) and trisodium citrate solution (1.0%, *w*/*v*) as both stabilizer and reducing agent were freshly prepared in ultrapure water. Sodium hydroxide stock solution at 0.1 M used for pH adjustment was prepared in ultrapure water. 4MP solution at 1.0×10^{-4} M and MAA solution at 1.0×10^{-4} M were daily prepared in ultrapure water for modification of AuNPs. Ammonium acetate buffer (pH 7.0) was prepared in ultrapure water. Fe(III) stock solution at 1.0×10^{-4} M was prepared in ultrapure water:HCl (25:1, *v*/*v*). DFO stock solution at 1.0×10^{-3} M was prepared in ultrapure water. Fe(III) and DFO solutions were stored at +4 °C. The stock solutions of metal ions (Na^+, Mn^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, As^{3+}, Ca^{2+}, Fe^{2+}, Hg^{2+}, and Cu^{2+}), anions (Cl^-, NO_3^-, and NO_2^-) and biomolecules {D(+)– glucose, tryptophan, lysine, trypsin, DL–alanine, L–leucine, and glycine} were prepared in ultrapure water and stored at +4 °C. The working solution of DFO for calibration curves of LC–MS/MS analyses was prepared daily at 10.0, 15.0, 20.0, 25.0, and 30.0 µM by diluting from the corresponding stock solution at 100.0 µM with ultrapure water.

3. Procedure of LC–MS/MS Method for Validation of DFO Detection

The working solutions of DFO at 10.0–30.0 µM were prepared from the corresponding stock solutions of 100.0 µM in ultrapure water. LC–MS analysis was performed on a UPLC–MS/MS equipment (Shimadzu, 20A) employing an injection volume of 20.0 µL. LC was equipped with a Rectek Ultra-AQ column (100 × 2.1 mm, 3 µm, C18). The column temperature was 40 °C; the injector temperature 4 °C, and the column flow rate 1.0 mL min^{-1}. The autosampler wash solution was MeOH:H_2O (1:1; *v*/*v*). HPLC separation was achieved using a binary gradient composed of mobile phase A {FA solution in H_2O, 0.1% (*v*/*v*)} and mobile phase B {FA solution in MeOH, 0.1% (*v*/*v*)}. The gradient used was as follows (all % values are *v*/*v*): from 0 to 1 min, 50% A; between 1 and 3 min, linear decrease to A 10%; between 3 and 5 min, a hold at A 10%. The mass spectrometer (Shimadzu, 8040) was functioned in the negative ion spray ionization (ESI–) mode. During operation, the mass analyser operated in the scan-only mode to obtain a mass spectrum employing selected ion monitoring (SIM) of m/z 561. The setting for MS operation were: nebulizing gas (N_2) flow, 3.0 mL min^{-1}; drying gas flow, 15.0 mL min^{-1}; gas temperature, 400 °C.

4. Supplementary Figures

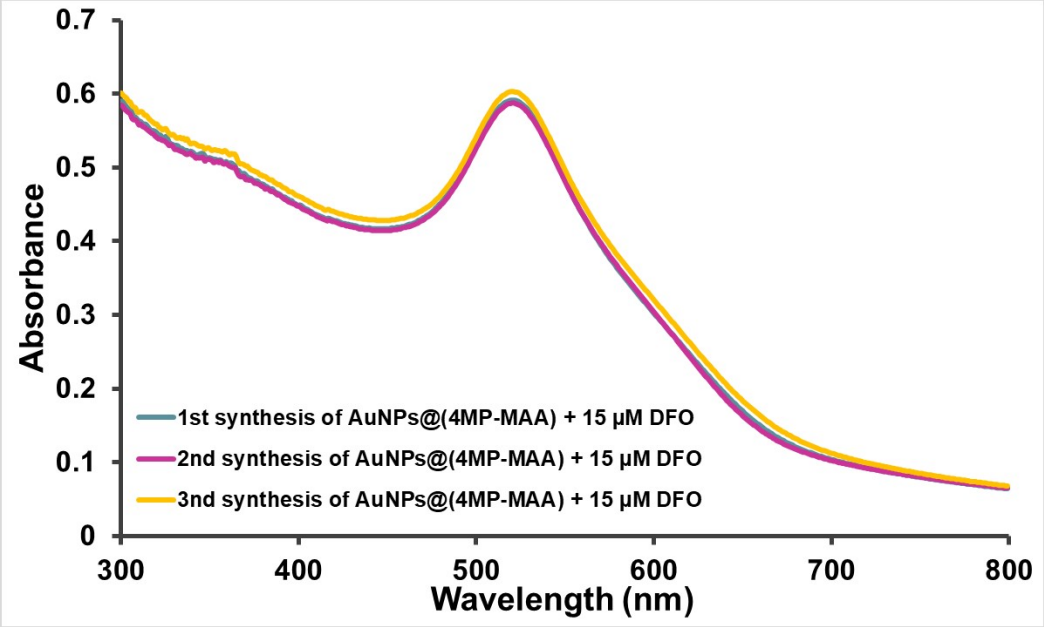


Fig. S1 UV-vis spectra of simultaneously prepared AuNPs@(4MP–MAA)/Fe(III) with DFO ([DFO]: 15.0 µM) (both synthesis and modification were made on the same day under the same conditions).

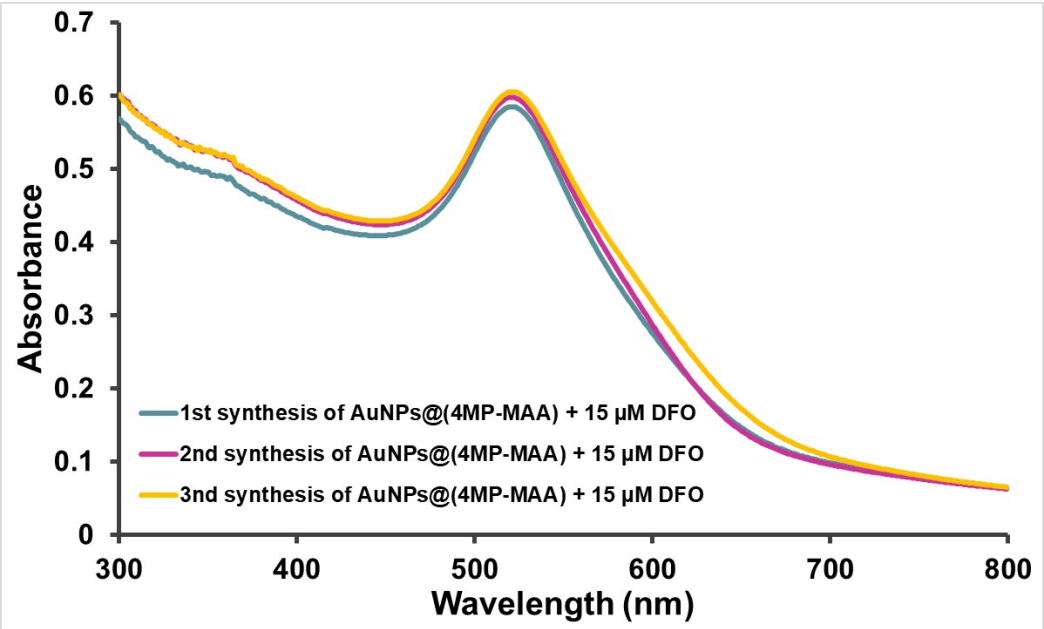


Fig. S2 UV-vis spectra of simultaneously prepared AuNPs@(4MP–MAA)/Fe(III) with DFO ([DFO]: 15.0 µM) (both synthesis and modification were made on different days under the same conditions).

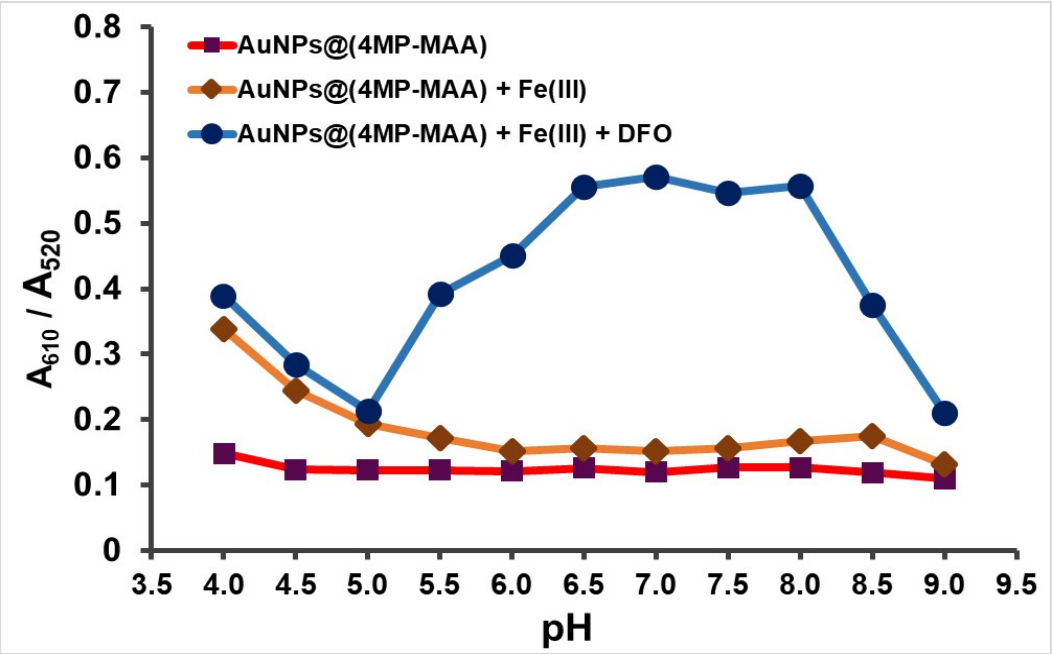


Fig. S3 Effect of pH (tris-HCl buffer) on the absorbance ratios of AuNPs@(4MP–MAA) (red squares), AuNPs@(4MP–MAA)/Fe(III) {[Fe(III)]: 1.0 µM, orange quadrilaterals}, and AuNPs@(4MP–MAA)/Fe(III)/DFO {[Fe(III)]: 1.0 µM, [DFO]: 40.0 µM, blue dots}.

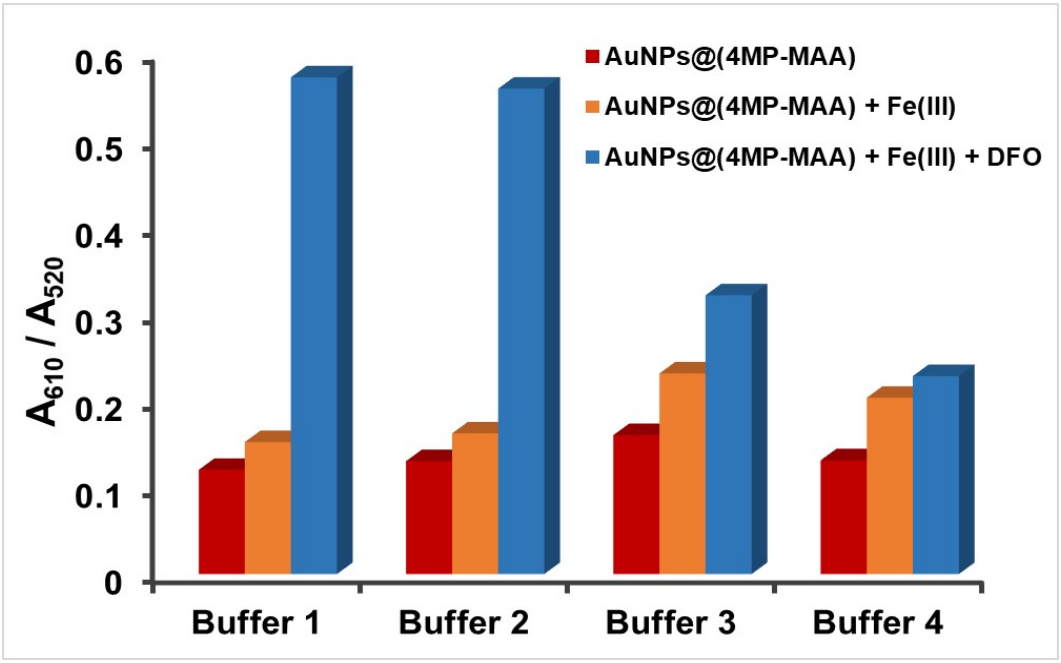


Fig. S4 Effect of different buffers (pH 7.0; 1: tris–HCl, 2: ammonium acetate, 3: phosphate, and 4: acetic acid–sodium acetate) on the absorbance ratios of AuNPs@(4MP–MAA) (red column), AuNPs@(4MP–MAA)/Fe(III) (orange column), and AuNPs@(4MP–MAA)/Fe(III)/DFO (blue column).

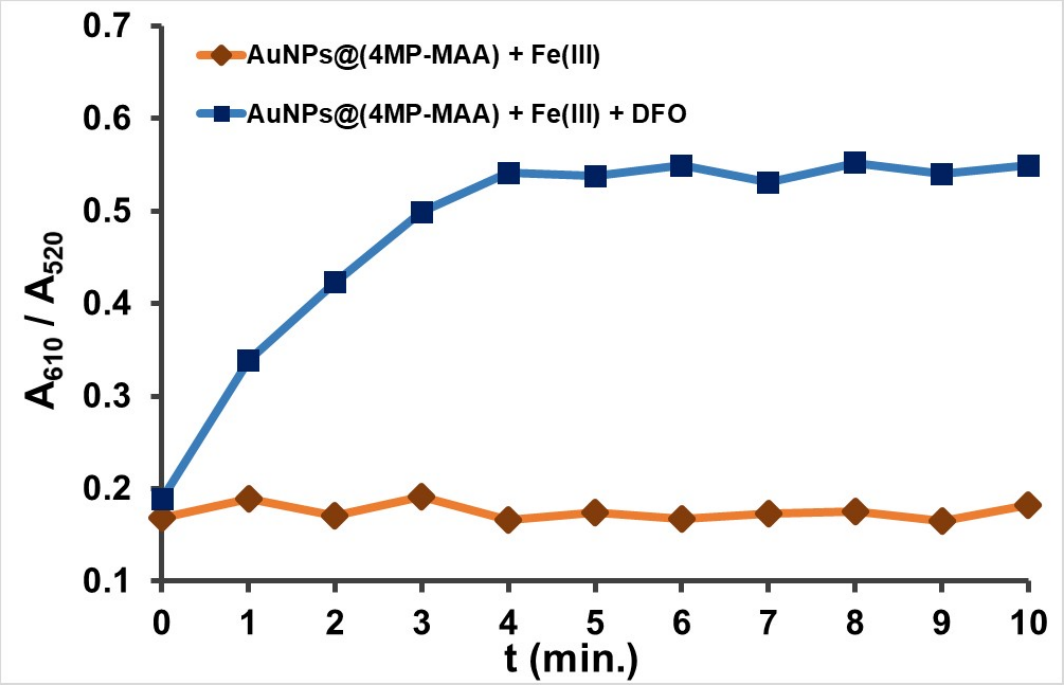


Fig. S5 Effect of incubation time on the absorbance ratios of the AuNPs@(4MP–MAA)/Fe(III) {[Fe(III)]: 1.0 µM, orange quadrilaterals} and AuNPs@(4MP–MAA)/Fe(III)/DFO {[Fe(III)]: 1.0 µM, [DFO]: 40.0 µM, blue squares}.

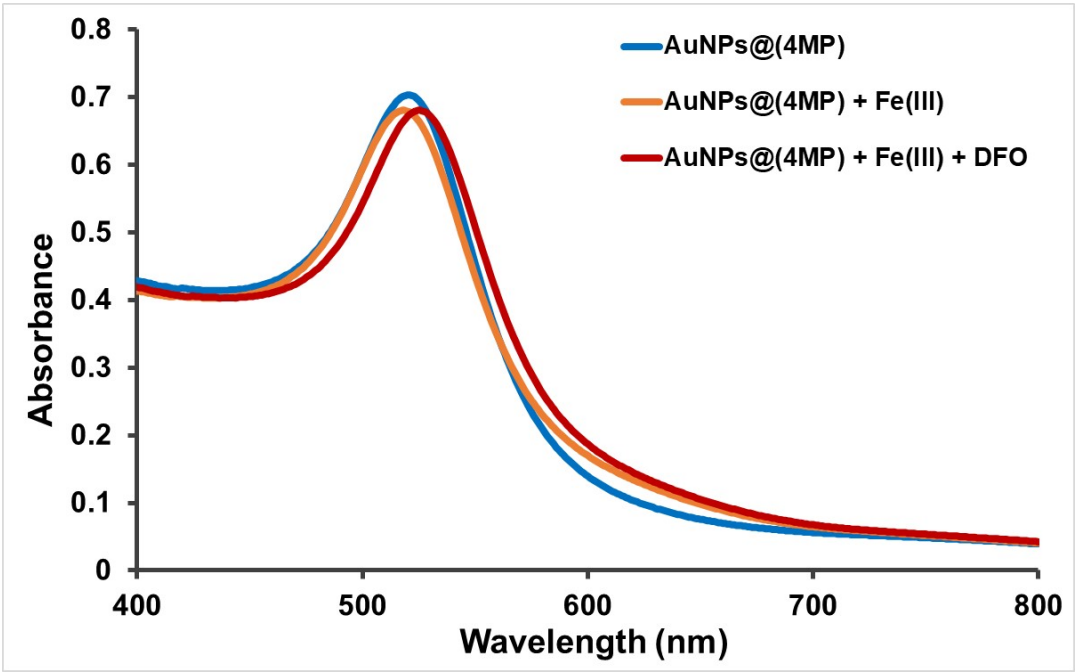


Fig. S6 UV–vis spectra of AuNPs@(4MP), AuNPs@(4MP)/Fe(III) ([Fe(III)]: 1.0 µM), and AuNPs@(4MP)/Fe(III)/DFO ([Fe(III)]: 1.0 µM, [DFO]: 40.0 µM) system.

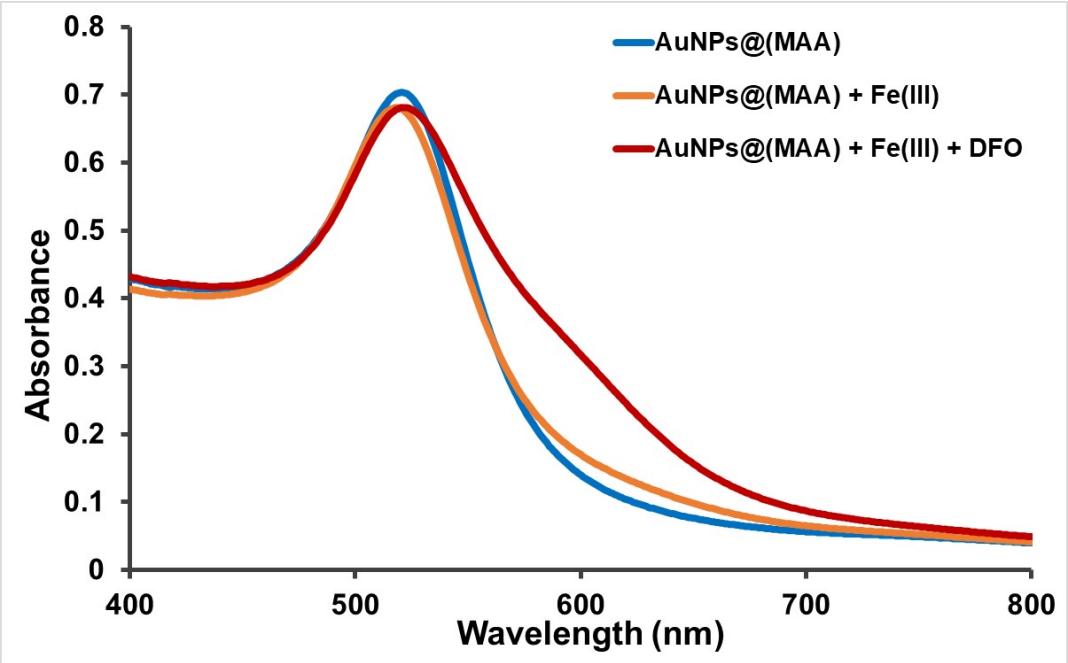


Fig. S7 UV–vis spectra of AuNPs@(MAA), AuNPs@(MAA)/Fe(III) ([Fe(III)]: 1.0 µM), and AuNPs@(MAA)/Fe(III)/DFO ([Fe(III)]: 1.0 µM, [DFO]: 40.0 µM) system.

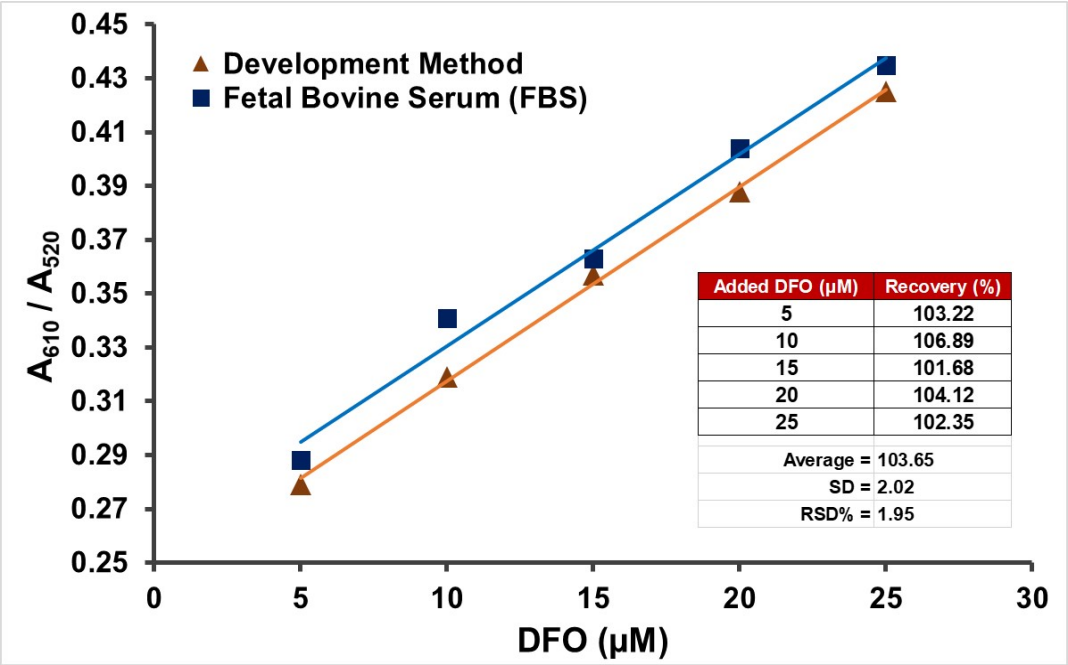


Fig. S8 Recovery of DFO from diluted Fetal Bovine Serum (FBS) {Inset: Recovery values obtained at different concentrations (5.0–25.0 µM) of DFO}.

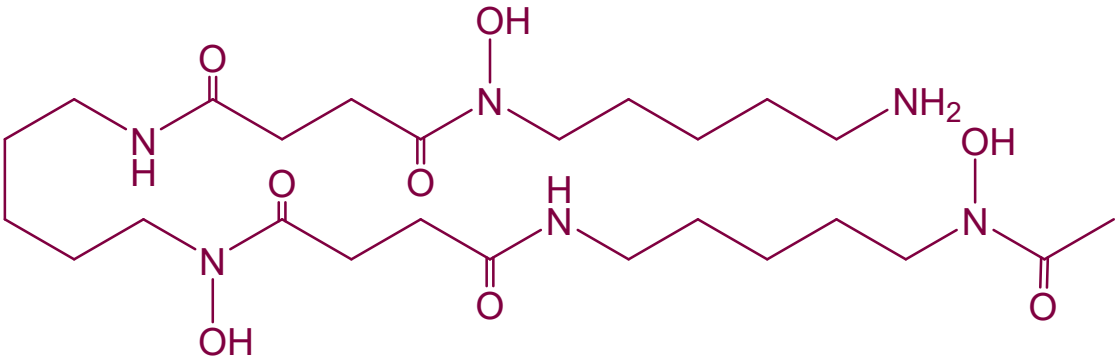
5. Supplementary Table

Table S1 Recovery (%) of Fe(III) ions and of DFO with the developed nanoprobe system in the presence of metal ions, common anions, and biochemical species.

Metal Ions			Anions			Biochemical Species		
Interferent	Recovery (%)		Interferent	Recovery (%)		Interferent	Recovery (%)	
	Fe(III)[a]	DFO[b]		Fe(III)[a]	DFO[b]		Fe(III)[a]	DFO[b]
Na(I)	103.95	96.30	Cl^-	98.48	100.95	D(+) Glucose	95.28	100.16
Mn(II)	104.30	101.44	CO_3^{2-}	97.72	104.34	Tryptophan	94.31	102.41
Mg(II)	105.19	103.85	NO_3^-	102.27	105.46	Lysine	97.87	102.57
Co(II)	103.09	102.41	NO_2^-	94.93	104.12	Trypsin	100.37	99.83
Zn(II)	101.81	103.69				DL-Alanine	104.92	99.19
Cr(III)	96.21	102.57				L-Leucine	95.45	100.32
As(III)	95.42	99.35				Glycine	100.36	102.73
Ca(II)	98.48	101.92						
Fe(II)	101.13	101.28						
Hg(II)	104.92	98.39						
Cu(II)	100.71	100.96						

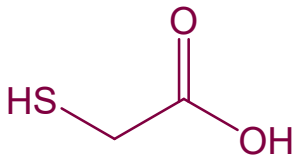
[a]Percentage recoveries of Fe(III) ions with the AuNPs@(4MP-MAA) sensing system in the presence of metal ions, common anions, and biochemical species. [b]Percentage recoveries of DFO with the AuNPs@(4MP-MAA) sensing system in the presence of metal ions, common anions, and biochemical species.

6. Molecular Structures



Structure 1 Molecular structure of deferoxamine (DFO, Molecular formula: $C_{25}H_{48}N_6O_8$, Molar mass: 656.79 $g.mol^{-1}$)

Structure 2 Molecular structure of 4-mercaptophenol (4MP, Molecular formula: C_6H_6OS, Molar mass: 126.18 $g.mol^{-1}$).



Structure 3 Molecular structure of mercaptoacetic acid (MAA, Molecular formula: $C_2H_4O_2S$, Molar mass: 92.12 $g.mol^{-1}$).