Electronic Supplementary Material (ESI) for RSC Advances.

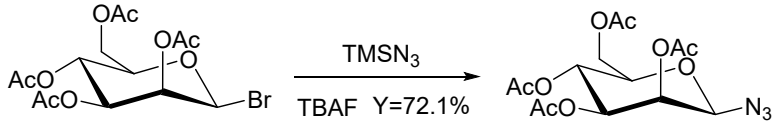
Supplementary materials

Self-assembled Nanovesicles based on Chiral Bis-H_8-BINOL for Fe^{3+} recognition and secondary recognition of cysteine by its complex

Content

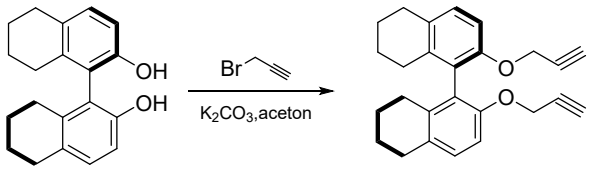
content

1.Synthesis of a



In a 100 mL aubergine flask, 1-bromo-2,3,4,6-tetraacetoxy-α-D-glucose (2.00 g, 4.86 mmol) was accurately weighed, the reaction system was sealed, and $TMSN_3$ (2.12 g, 18.48 mmol) and TBAF (5.07 mL, 18.48 mmol) were added under the protection of argon gas, 15 mL of THF was added, and the reaction was carried out at The reaction was carried out at room temperature for 24 h. The complete reaction of the raw materials was shown by TLC (EA:PE=1:4), and the solvent was evaporated by rotary evaporator, and then separated by column chromatography to obtain 1.31 g of white solid, which was obtained in 72.1% yield.^{1}H NMR (400 MHz, DMSO-d_6) δ 5.30 (t, J = 9.6 Hz, 1H), 5.11 (d, J = 8.9 Hz, 1H), 4.96 (t, J = 9.5 Hz, 1H), 4.80 (t, J = 9.3 Hz, 1H), 4.17 – 4.02 (m, 3H), 2.01 (d, J = 4.7 Hz, 12H).^{13}C NMR (101 MHz, DMSO-d_6) δ 170.10, 169.33, 169.20, 139.25, 86.39, 73.66, 72.93, 71.98, 70.41, 67.96, 67.16, 61.81, 60.60, 20.59.

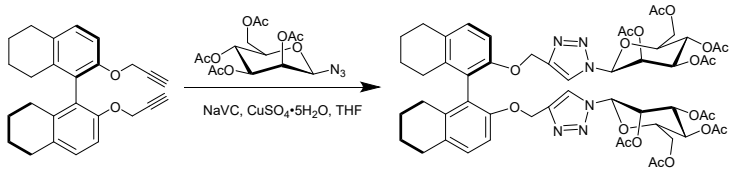
2.Synthesis of b



(R) -H_8BINOL (2.0 g, 6.79 mmol), potassium carbonate (1.97 g, 14.3 mmol) and acetone (15.0 mL) as solvent were added to a 100 mL three-neck flask. 3-Bromopropyne (1.46 mL, 16.98 mmol) was slowly added to the three-necked flask and stirred at room temperature for 5-7 min before the reaction system was transferred to an oil bath at 70 °C and refluxed for 13 h. The reaction system was then purified by TLC. The reaction was quenched when TLC detection (EA:PE=1:4) showed complete reaction of the raw material. The system was cooled to room temperature and the reaction liquid was filtered through a recirculating pump and the filtrate was washed three times with acetone. About 200-300 mesh of silica was added to the filtrate and the solvent was dried on a rotary evaporator to give a yellow-brown powder. Column chromatography using petroleum ether and ethyl acetate as eluents (V(PE):V(EA) = 20:1) yielded 1.56 g of yellow-brown solid in 61.2% yield.^{1}H NMR (400 MHz, DMSO-d6) δ 7.00 (d, J = 8.5 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 4.60 (d, J = 4.0 Hz,

2H), 3.41 (d, J = 1.8 Hz, 1H), 2.56 – 2.46 (m, 4H), 1.60 (dd, J = 26.4, 5.5 Hz, 4H).^{13}C NMR (101 MHz, DMSO-d6) δ 152.22, 136.02, 129.75, 128.42, 125.75, 110.63, 79.93, 77.53, 55.44, 39.71, 28.83, 26.76, 22.74.

3.Synthesis of *R*-β-D-**1** probe.



R-2,2'-bis(prop-2-yn-1-yloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene (0.20 g, 0.54 mmol) and 1-azido-2,3,4- triacetoxy-5-acetoxymethyl-D-glucose (0.44 g, 1.19 mmol). Under argon protection, 5 mL of tetrahydrofuran was added to the system. The ice bath was stirred for a few minutes to dissolve it completely, next, sodium ascorbate (0.24 g, 1.18 mmol) and anhydrous copper sulfate (0.13 g, 0.54 mmol) were accurately weighed and dissolved in 4 mL of deionized water, shaken well, and when the mixed solution turned to an earthy yellow color, it was added to the reaction system. The system was reacted for 10 h at room temperature and TLC was performed (PE:EA = 4:1). The reaction was quenched by adding 10 mL of ice water to the reaction system and the aqueous phase was extracted three times with 30 mL of dichloromethane. The organic phases were then combined, washed once with saturated NaCl solution and dried with anhydrous magnesium sulfate for 30 min. After filtration and rotary evaporation of the solvent, it was separated by column chromatography (PE:EA = 1:1). About 0.55 g of white solid was obtained in 91.2% yield.^{1}H NMR (400 MHz, DMSO-d6) δ 8.03 (s, 1H), 6.95 (s, 2H), 6.31 (d, J = 8.6 Hz, 1H), 5.59 – 5.46 (m, 2H), 5.15 (t, J = 9.5 Hz, 1H), 5.05 – 4.92 (m, 2H), 4.19 – 3.97 (m, 3H), 2.04 – 1.96 (m, 8H).^{13}C NMR (101 MHz, DMSO-d6) δ 170.06, 169.43, 168.42, 152.95, 144.25, 136.23, 129.61, 128.45, 126.11, 123.10, 111.04, 83.90, 73.49, 72.30, 70.34, 67.73, 61.92, 61.57, 40.36, 39.10, 28.88, 26.79, 22.73, 20.55, 20.35, 19.85.

4. ^{1}HNMR, ^{13}CNMR of a (DMSO-D_6)

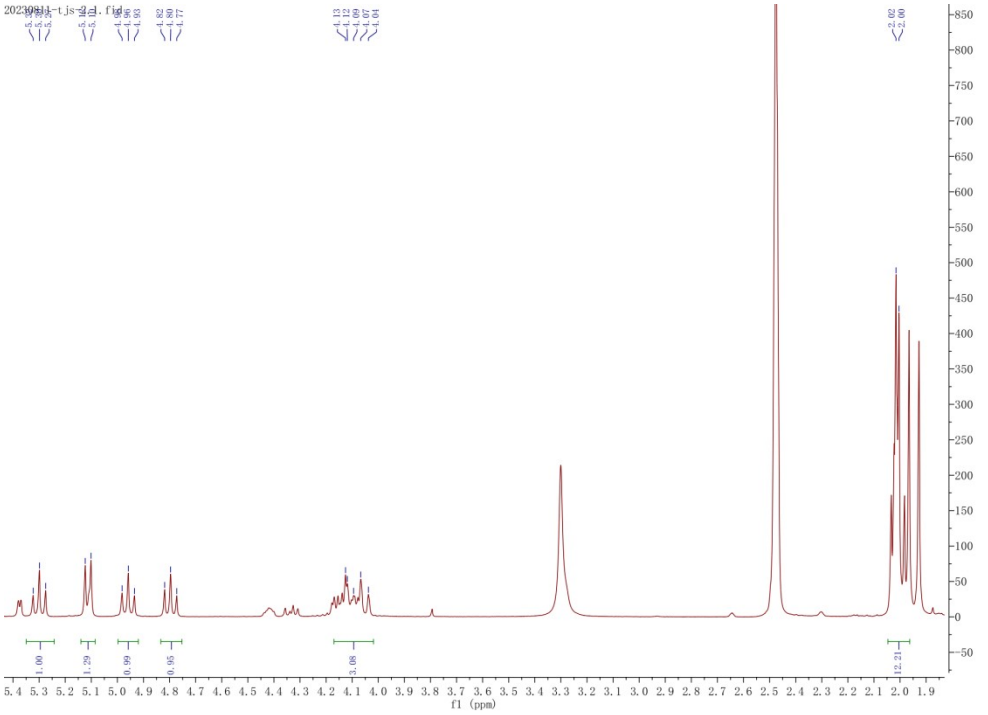


Figure S1 ^{1}H NMR of a (DMSO-d_6)

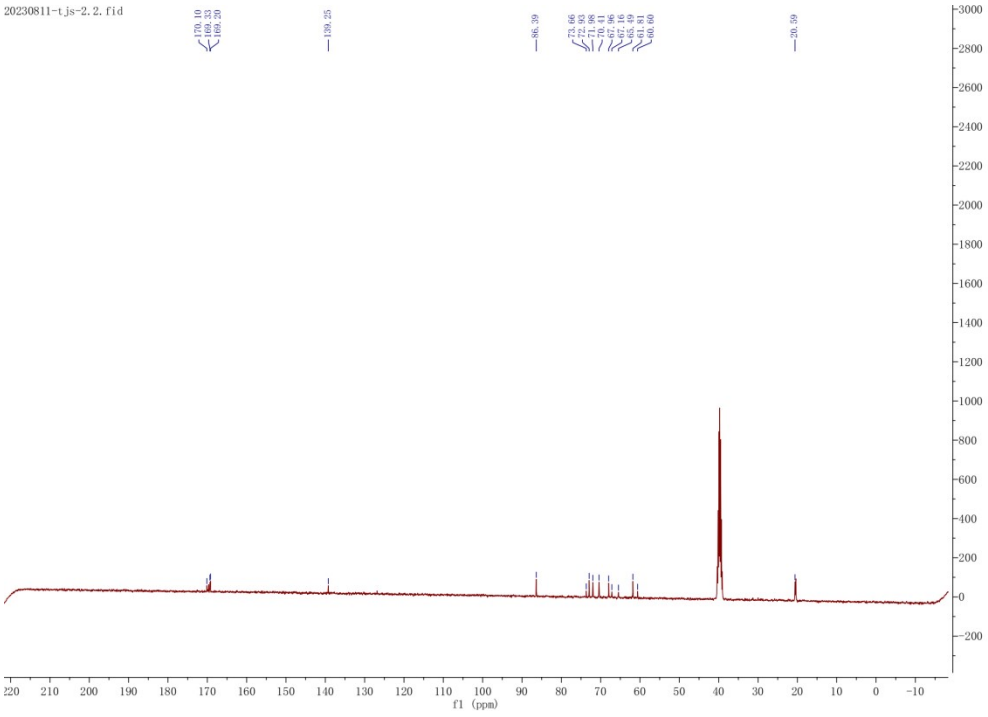


Figure S2 ^{13}C NMR of a (DMSO-d_6)

5. ^{1}HNMR, ^{13}CNMR of b (DMSO-D_6)

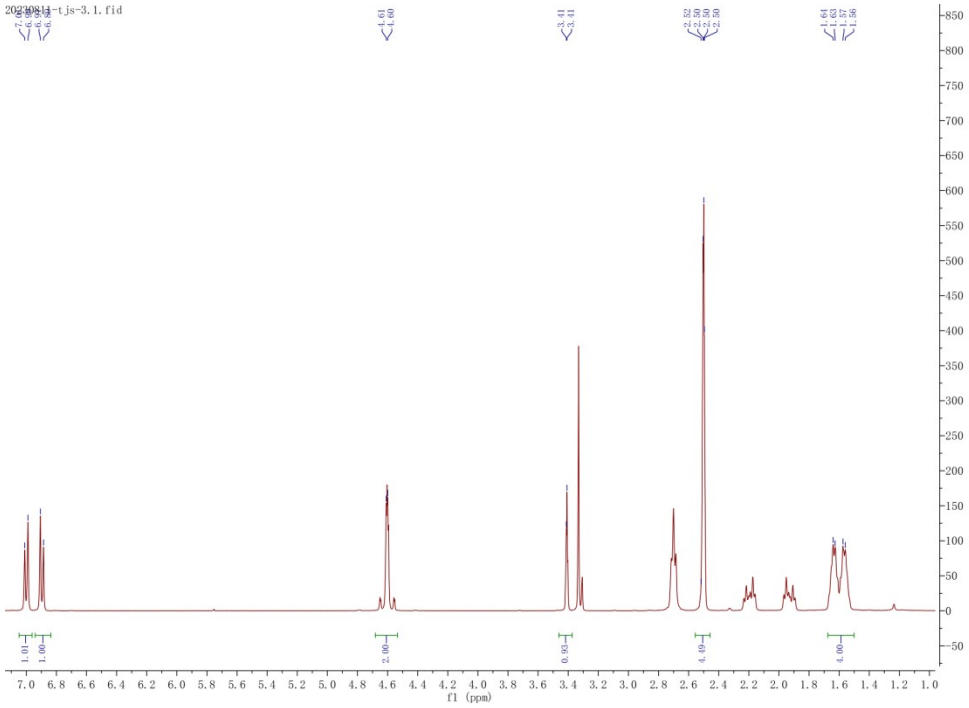


Figure S3 ^{1}H NMR of b (DMSO-d_6)

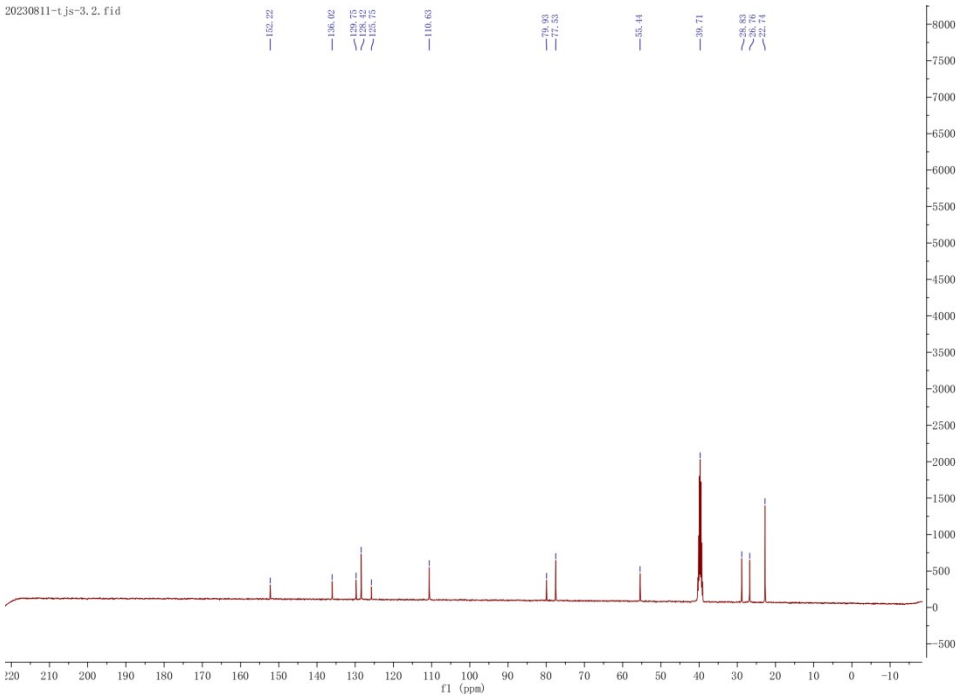


Figure S4 ^{13}C NMR of b (DMSO-d_6)

6. ^{1}HNMR, ^{13}CNMR of *R*-β-D-**1** (DMSO-D_6)

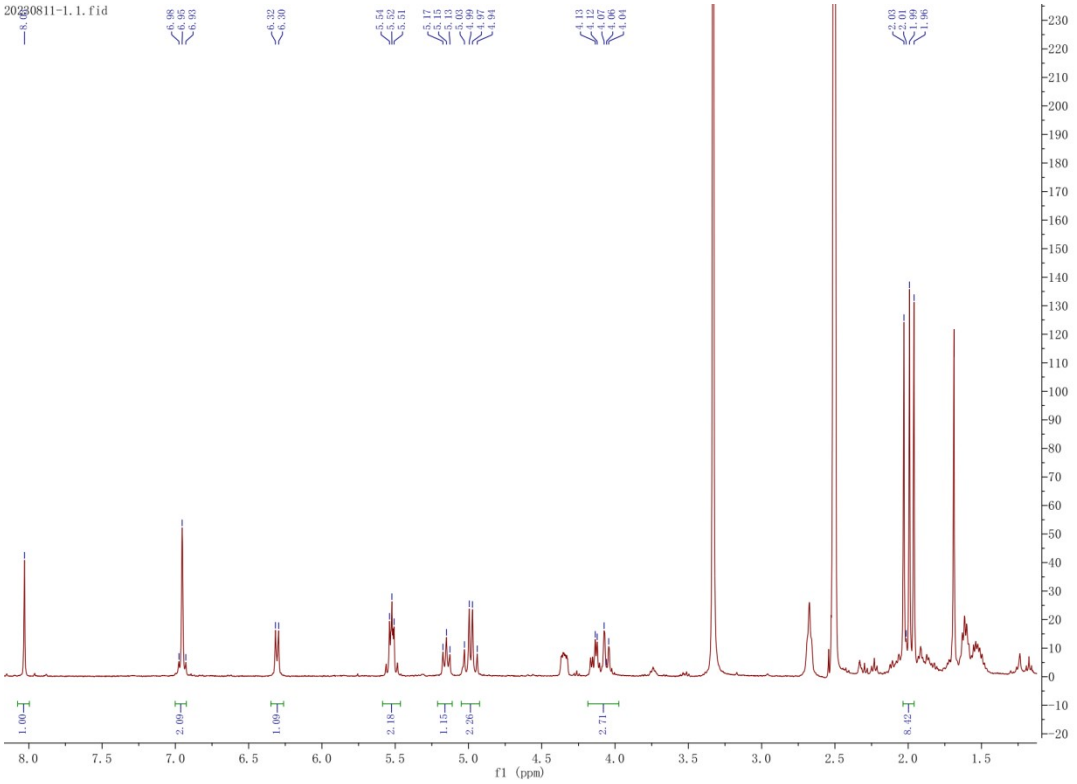


Figure S5 ^{1}H NMR of *R*-β-D-**1** (DMSO-d_6)

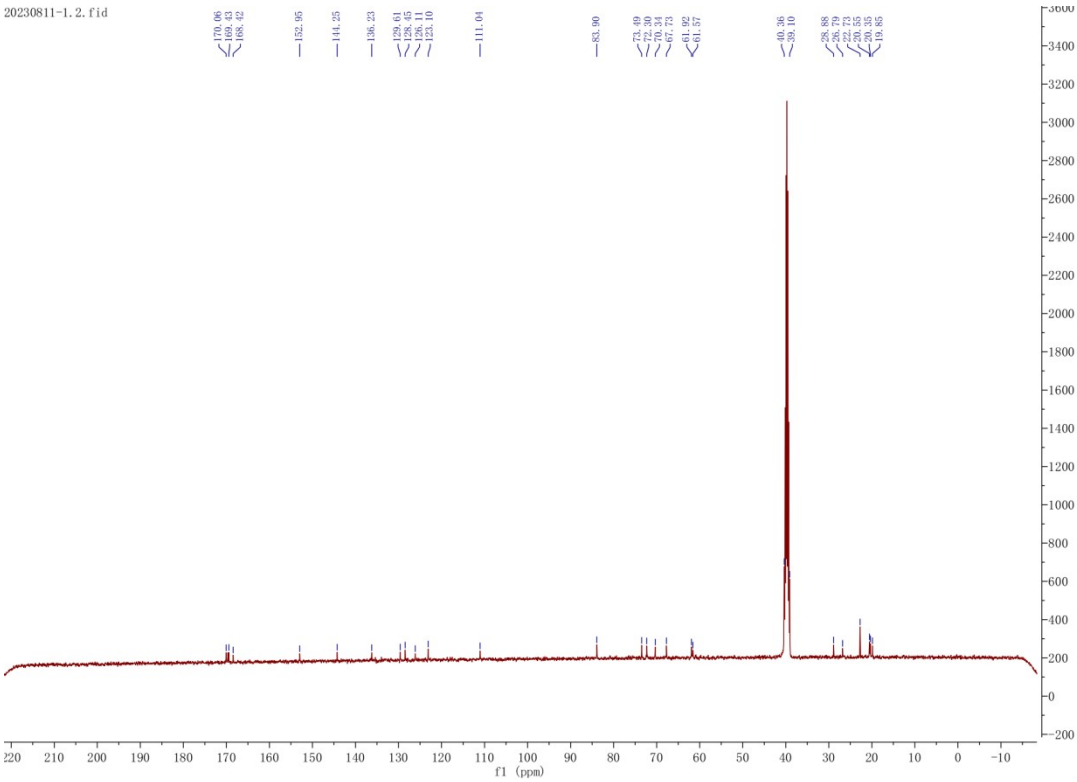


Figure S6 ^{13}C NMR of *R*-β-D-**1** (DMSO-d_6)

7.Metal Ion Competition Study

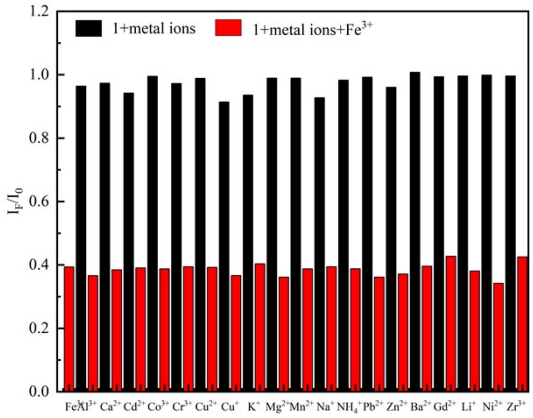


Figure S7. Black bars in the graph indicate the addition of 5.0 eq of different metal ions (20 μM in CH_3OH) in *R*-β-D-**1** solution; red bars in the graph indicate the addition of competing metal ions in the presence of Fe^{3+}. I_F/I_0 indicates the degree of fluorescence burst. The I_0 indicates the fluorescence intensity of *R*-β-D-**1** only, and the I_F indicates the fluorescence intensity of the mixture of competing metal ions and Fe^{3+}

8. Ion fluorescence recognition

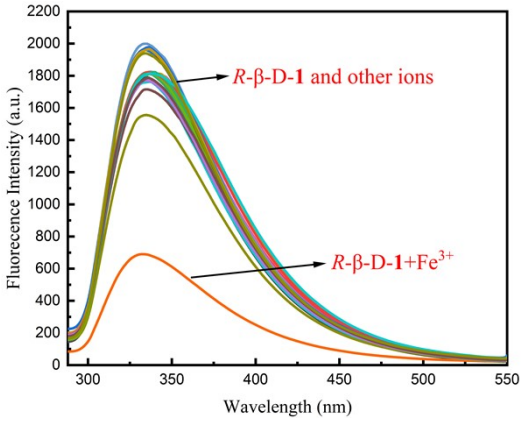


Figure S8. Fluorescence spectra of (*R*-β-D-**1**) (20 μM, MeOH solution) in the presence of different ions (e.g.,Ba^{2+}, Mn^{2+}, Cu^{+}, Ca^{2+}, K^{+}, Co^{3+}, Cr^{3+}, Zn^{2+}, Al^{3+}, Mg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Gd^{3+}, Li^{+}, Na^{+}, NH_4^{+}, Ni^{2+}, and Fe^{3+}) (*R*-β-D-**1** + 5 equiv ions,).

9. Amino acid fluorescence recognition

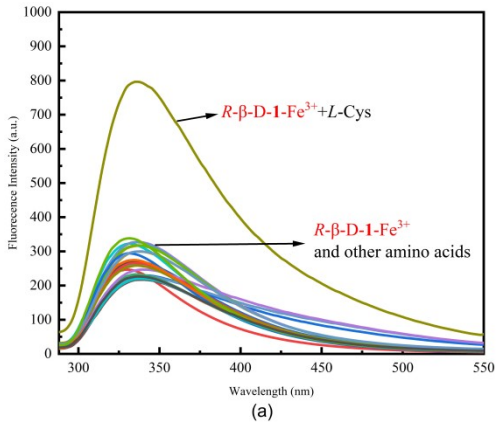


Figure S9. Fluorescence of *R*-β-D-**1**-Fe^{3+} (20μM in CH_3OH, 10 equiv Fe^{3+}) in the presence of 10 equiv of amino acids of different conFigureurations Ile, Phe, Ala, Arg, Ser, His, Pro, Asp, Lys, Gly, Val, Asn, Met, Gln, Thr, Glu, Leu and Cys Spectrogram.

10. *R*-β-D-**1**-Fe^{3+} binding constants to L-Cys and affinity calculations.

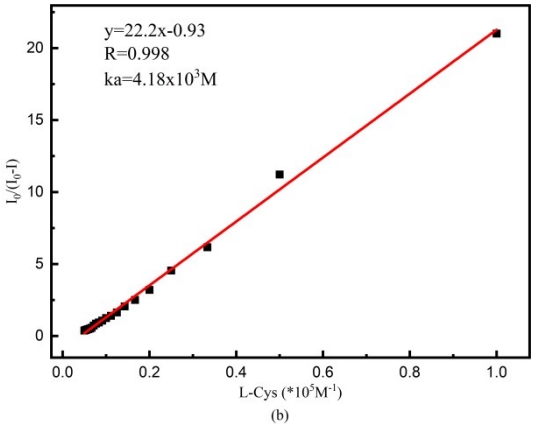


Figure S10, Binding constants and affinity calculations on *R*-β-D-**1**-Fe^{3+} with L-Cys.

11. Fluorescence test sample configuration method

11.7 mg of probe *R*-β-D-**1** in a 10 mL volumetric flask, add chromatographic methanol to dissolve and quantify to 10 mL, at this time, the concentration of the test masterbatch is 0.001 M. Next, the masterbatch will be diluted to 2.0×10^{-5} M, and taken at any time when needed.
Commonly used ion configuration ($BaCl_2$, $MnCl_2$, CuCl, $CaCl_2$, KCl, $CoCl_3$, $CrCl_3$, $ZnCl_2$, $AlCl_3$, $MgCl_2$, $PbCl_2$, $CuCl_2$, $CdCl_2$, $GdCl_3$, LiCl, NaCl, NH_4Cl, $NiCl_2$, $FeCl_3$ configured into a

concentration of 0.1 M) (Methanol solution, need to be ready to use, room temperature 25 ℃, take 2mL test solution added to 3.5mL high transparent quartz fluorescence cuvette, add 2μL of ions to be tested, fluorescence test).

Commonly used amino acid configuration (L-phenylalanine, L-histidine, L-lysine, L-alanine, L-arginine, L-serine, L-methionine, L-leucine, L-glycine, L-valine, L-aspartic acid, L-glutamine, L-threonine, L-glutamate, L-proline, L-aspartic acid, L-cysteine configured into 0.05M deionized water) (The solution should be ready to use, room temperature 25℃, take 2mL of the test solution and add it into a 3.5mL high transparent quartz fluorescence cuvette, add 4μLFe3+ ions, then add 8μL of the amino acid to be tested for the fluorescence test).