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Supplementary Information

Highly sensitive colorimetric sensor for the detection of Mn²⁺

based on Supramolecular silver nanoparticle clusters

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Experimental Section

All chemicals and solvents unless otherwise specified were analytical grade, and triply distilled water were used throughout. AgNO₃ and NaBH₄were purchase from Shanghai Chemical Factory, China. Metal ions (CuCl₂, CaCl₂, ZnCl₂, CrCl₃, CdCl₂, MnCl₂, FeCl₂, PbCl₂, CoCl₂, and HgCl₂) were obtained from Beijing Chemical Corp. (Beijing, China). All salts standards were dissolved in triply distilled water and stored at room temperature.

UV-vis absorption spectra were acquired on a S-3100 UV-vis spectrometer. IR spectra were measured with a NEXUS FT-IR spectrometer (Thermo Nicolet Co.), Transmission electron, micrograph (TEM) was recorded by a JEOL-JEM 2010 electron microscope operating at 200 kV.

Preparation of β-CD-ADM-Ag NPs clusters:

1 mL of 10^{-2} mol/L of silver nitrate (AgNO₃) aqueous solution was added into 96 ml of triply distilled water, and then 10 mg of sodium borohydride (NaBH₄) were added into the silver nitrate solution with stirring for 20 min, the color of nanoparticle solution turn golden yellow, and then 1 mL of 1 mM concentrated aqueous solution of β -CD was added rapidly into solution and stirred for another 2 h at room temperature to get β -CD Ag NPs.

1 mL of 10^{-3} mol/L ADM aqueous solution was added into 100 mL β -CD Ag NPs, then the reaction mixture was centrifuged at 3000 rpm for 10 min for three times, the dispersed in distilled water to get β -CD-ADM Ag NPs.

Colorimetric assay for Mn²⁺:

The colorimetric tests of β -CD-ADM Ag NPs responding to metal ions were operated as follows: 0.5 mL of 1mM aqueous solution of various metal ions was added to 1.5 mL of β -CD-ADM Ag NPs and after combining 5 min, the solutions were test.

Supplementary figures



Fig.S1 FT-IR of ADM (A) and β -CD (B) and β -CD-ADM-Ag NPs (C), the framework vibration of β -CD remained unchanged, which demonstrated that β -CD was successfully modified on the surface. After in the presence of ADM, the characteristic peaks of methylene at 2912 cm⁻¹ and 2840 cm⁻¹ appeared in β -CD-ADM Ag NPs, which indicated that the ADM has been successfully attached onto β -CD.



Fig.S2 The stability of silver nanoparticle clusters (β -CD-ADM-Ag NPs) solution with various pH value (A) and time (B). (The wavelength is 400 nm). The resulting Ag NPs showed very good stability in water without any apparent aggregation for two weeks



Fig.S3 (A) photographic images and (B) The UV-vis spectra solution of β -CD Ag NPs in the presence of 0.1 mM different transition metal ions. Inset: the absorbance ratio R of β -CD-ADM Ag NPs solution in the presence of 1 mM different metal ions, the solvent used in the experiment is triply distilled water. Monitoring was started 5 min after addition of metal ions. It proved that the β -CD Ag NPs do not have selective for Mn²⁺.



Fig. S4 (A)The colour change of β -CD-ADM-Ag NPs s solution after adding different concentrations of Mn²⁺ from 1×10⁻³ M to 1×10⁻⁸M in Yangtze River water, and (B) the UV-vis absorption spectra of β -CD-ADM-Ag NPs solution after adding different concentrations of Mn²⁺. The concentration of Mn²⁺ is (1) 10⁻³ M; (2) 5×10⁻⁴ M; (3) 10⁻⁴ M; (4) 5×10⁻⁵ M; (5) 10⁻⁵ M; (6) 5×10⁻⁶ M; (7) 10⁻⁶ M; (8) 5×10⁻⁷ M; (9) 10⁻⁷ M; (10) 5×10⁻⁸ M; (11) 10⁻⁸ M. Insets: absorption ratios. The detection limit for Mn²⁺ ions was 5×10⁻⁶ M in Yangtze River water.