Electronic Supplementary Information

Dual Emitting Quantum Dot Complex Nanoprobe for Ratiometric and Visual Detection of Hg²⁺ and Cu²⁺ ions

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Experimental Section

A. Materials: Manganese acetate tetrahydrate (Merck), zinc acetate dihydrate (Merck), sodium sulphide (Merck), 1 M methylamine in methanol (Sigma-Aldrich), salicylaldehyde (Sigma-Aldrich), mercury acetate (Merck), copper acetate (Merck), lead acetate (Merck), cobalt acetate (Merck), nickel acetate (Merck), cadmium acetate (Merck), sodium acetate (Merck), methanol (Merck) were purchased and used directly without any purification.

B. Synthesis of Mn²⁺-doped ZnS Qdots: The synthesis of Mn²⁺-doped ZnS Qdots was performed using a reported protocol.^[1-2] Concisely, 5.0 mM of sodium sulphide was added into a 50 mL aqueous solution containing of the mixture of 5.0 mM of zinc acetate dihydrate and 0.75 mM of manganese acetate tetrahydrate. The subsequent mixture was refluxed for 4 h under continuous stirring at 100 °C. The so-obtained white colloidal particles were centrifuged with a speed of 12,000 rpm for 10 min. The centrifuged pellet was thoroughly washed and redispersed into the same amount of water and centrifuged again with same experimental conditions. The washing cycle was repeated (in the presence of methanol) and finally the pellet was dispersed in 200.0 mL of methanol. The so obtained colloidal dispersion was used for further experiments. The Qdots were characterized by using fluorescence, UV-vis, TEM and XRD analyses.

C. Preparation of MSA Solution: The synthesis of MSA Ligand was carried out following a reported procedure. ^[3-4] Briefly, the addition of 4.0 mmol of methylamine into a solution of 2.0 mmol of salicylaldehyde (in 20.0 mL methanol) resulted in yellow color mixture, which was kept for 6 h under stirring condition at 25 °C. Then, the resulting MSA ligand was purified by column chromatographic technique.

D. Synthesis of Dual-Emitting QDC: The dual-emitting QDC was synthesized by addition of 150.0 μ L of 5.0 mM of MSA (methanol) to the 10.0 mL methanolic dispersion of Mn²⁺ doped ZnS Qdots (with absorbance of 0.03 at 355 nm). The resulting mixture was centrifuged at a speed of 12000 rpm and the pellet was further redispersed in the equal amount of solvent. The optimum amount of the MSA ligand was found to be 75.0 μ M for the fabrication of purple colored dual - QDC. The dual-emitting QDC was characterized by using fluorescence, UV-vis, TEM and XRD analyses.

E. Heavy Metal Ion Sensing: The heavy metal ion sensing of QDC was performed following individual sequential addition of the solutions of 1.0 mM Hg²⁺ and Cu²⁺ ions (as their acetate salts) to 3.0 mL dispersion of QDC (having absorbance of 0.03 at 355 nm). The limit of detection (LOD) was calculated by using $3\sigma/k$ plot. The changes in the luminescence properties (such as color, intensity ratio, chromaticity and hue) of the QDC were monitored to detect the mentioned heavy metal ions.

F. Selectivity Experiment: The selectivity experiment was carried out by using higher concentration (83.33 μ M) of interfering metal ions compared to Hg²⁺ (16.67 μ M) and Cu²⁺ ions (13.33 μ M). The 5.0 mM acetate salts of Pb, Ni, Co, Cd, Mn, Na were added to 3.0 mL of QDC (having absorbance of 0.03 at 355 nm) separately so that the final concentration of interfering ions were to be 83.33 μ M while 16.67 μ M of Hg²⁺ ions and 13.33 μ M of Cu²⁺ ions were used for the selectivity experiment. Emission spectra and corresponding intensity ratio were monitored to describe selectivity of the QDC.

G. Instruments: Transmission electron microscopy (TEM; JEOL JEM 2100F, maximum accelerating voltage: 200 kV) was used to analyze the size and lattice fringe of the materials. TEM and inverse fast Fourier transform analyses were done by using Gatan Digital Micrograph software. Brucker D2 Advance X-ray diffractometer was used to record the diffraction patterns of the materials. HORIBA Jobin Yvon FluoroMax-4 spectrofluorimeter and Perkin Elmer LAMBDA 750 UV–vis spectrophotometer were used to record the luminescence and absorption spectra of the materials, respectively. OSRAM color calculator (CIE-1931) was used to calculate the chromaticity of the samples. Hue analysis was performed by using Image-J software following earlier protocols.²



Fig. S1. UV-vis absorption spectra of (i) Mn²⁺ doped ZnS Qdots and (ii) the dual-emitting QDC.



Fig. S2. (A) Transmission electron microscopy (TEM) image (scale bar-20 nm), **(B)** particle size distribution, **(C)** high resolution TEM image (scale bar = 5 nm) and corresponding inverse fast Fourier transformed image (inset), and **(D)** powder x-ray diffraction (XRD) pattern of Mn^{2+} doped ZnS Qdots.



Fig. S3. (A) Transmission electron microscopy (TEM) image (scale bar = 20 nm), **(B)** particle size distribution, **(C)** high resolution TEM image (scale bar = 5 nm) and corresponding inverse fast Fourier transformed image (inset), and **(D)** powder x-ray diffraction (XRD) pattern of the dualemitting QDC.



Fig. S4. Photostability results of the dual-emitting QDC as monitored by the variation of intensity (Y-axes) with time with respect to emission maxima at (A) 600 nm and (B) 430 nm.



Fig. S5. UV-vis absorption spectra of QDC (A) (i) in absence and (ii) presence of Hg^{2+} and (B) (i) in absence and (ii) presence of Cu^{2+} ions.



Fig. S6. (A) Emission spectra ($\lambda_{ex} = 355 \text{ nm}$) of (i) QDC and (ii) Hg²⁺ ion added dual-emitting QDC before centrifugation, (iii) the pellet obtained after centrifugation and redispersion into same amount of solvent and (iv) of the supernatant after centrifugation. (B) Emission spectra ($\lambda_{ex} = 355 \text{ nm}$) of (i) QDC and (ii) Cu²⁺ ion added dual-emitting QDC before centrifugation, (iii) the pellet obtained after centrifugation and redispersion into same amount of solvent and (iv) of the supernatant after same amount of solvent and (iv) of the pellet dual-emitting QDC before centrifugation, (iii) the pellet obtained after centrifugation and redispersion into same amount of solvent and (iv) of the supernatant after centrifugation.



Fig. S7. Emission spectra of MSA in (i) absence and (ii) presence of Zn^{2+} ions.

Ref. no.	Used optical nanoprobe	Detected ion	Linear range/LOD	Advantages	Disadvantages
This Work	Dual emitting QDC	Hg^{2+}	0.67-3.33 μM/ 85.5 nM	Ratiometric (I_{430}/I_{600}) , luminescence color, chromaticity and hue	
		Cu ²⁺	0.67-5.33 µM/ 34.9 nM	based detection of Hg^{2+} and Cu^{2+} ions	
5	Au-Ag NCs	Cu ²⁺	20-600 nM/7 nM	Ratiometric detection	Expensive and
		Hg^{2^+}	20-2000/ 5 nM		complicated fabrication
6	CD/CD conjugates	$\begin{array}{c} Cu^{2+} \\ Hg^{2+} \end{array}$	0–3.2 μM/0.05 μM 0–8.5 μM/0.08 μM	Ratiometric detection	Non-radiative energy transfer and complicated fabrication
7	CDs mixed with CdTe/CdS Qdots	Cu ²⁺	0-2.5 μM/ 38 nM	Ratiometric detection	Toxicity and Non-radiative energy transfer
8	C-NP and rhodamine B dye hybrid	Hg^{2+}	0-6 µM /45 nM	Ratiometric detection	Toxicity and Non-radiative energy transfer
9	Coumarin derivatives	Hg ²⁺	0–5 mM/ 27 nM	Ratiometric detection	Toxicity and complicated fabrication

Table S1. Tabulated form of the comparison of different optical nanoprobes for ratiometric sensing of Hg^{2+} and Cu^{2+} ions.

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