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Supporting Information

Environmentally benign and Cost-Effective Synthesis of Water Soluble Red Light Emissive Gold Nanoclusters: Selective and Ultra-Sensitive Detection of Mercuric Ions

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Experimental Section:

Materials

Sodium hydroxide (NaOH), Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) and all other metal ions were purchased from Sigma-Aldrich and used as-received during detection of their respective metal ions. Wheat flour was purchased from local market.

Synthesis of fluorescent Gold Nanoclusters (AuNCs):

All the glass wares were first washed with aqua regia solution and then rinsed with copious amounts of ultrapure water, before use. To synthesize AuNCs, first required amount of wheat flour (300 g) was added in NaOH solution and stirred vigorously until homogeneous solution appeared. Hence, $HAuCl_4.3H_2O$ solution was added to the solution with vigorous stirring and maintained at 50 °C until the solution color changes from yellow to deep brown. To inhibit the gelatinization of starch in wheat flour, this process performed under 60 °C. To obtain, highly red emissive AuNCs the concentration of NaOH was varied and we found that 25 mM NaOH-5 mM gold concentration yields best AuNCs. The cluster formation was confirmed by intense red emission under table top UV light (365 nm excitation). Furthermore, the deep brown solution was first filtered to remove larger particles and then dialyzed against double distilled water for 48 h using a dialysis membrane (molecular weight cutoff of 11 kDa) to obtain purified product. The purified clusters were then stored at 4 °C and dark condition for future use.

Metal ion Sensing:

To detect Hg^{2+}, various concentrations of Hg^{2+} were added to aqueous solutions of AuNCs and the fluorescence emission of AuNCs were monitored. A series of metal ions including Na^+, K^+,

Mg^{2+}, Zn^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+} (10 mM) were added to AuNCs in solution to evaluate the selectivity.

Characterization Techniques:

The cluster formation was confirmed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV-vis absorption and fluorescence spectroscopy.

Microscopy

The TEM images of AuNCs before and after addition of Hg^{2+} were characterized through JEM-ARM200F atomic resolution analytical microscope. The samples for TEM measurements were prepared by casting a small drop of dilute solution on a carbon-coated copper grid, allowed to dry in air, and finally dried in vacuum at 30 °C.

Spectroscopy

The UV-vis absorption spectra were measured on a UV-vis spectrophotometer (JASCO Corporation, V-650). The fluorescence spectra of AuNCs were collected using a sealed quartz cuvette of 1 cm path length and the emission was recorded in a fluorescence spectrophotometer (PerkinElmer, LS-55) with a He-Cd laser source. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo UK, with a monochromatic Al Kα X-ray source.

Quantum yield (QY) measurement

QYs of the AuNCs were determined by calculating the integrated fluorescence intensities of AuNCs and reference dye (rhodamine 6G solution in ethanol, QY = 94%).[1] The value of QY was calculated according to the following equation:[2,3]

$$QY_{sample} = QY_{std.} [(I/A)_{sample} \times (A/I)_{std.}] (\eta^2_{sample}/ \eta^2_{std.})$$

where A denotes absorbance at the excitation wavelength, η is the refractive index of solvent and I is the integrated emission intensity calculated from the area under the emission peak on the same wavelength scale. The absorbance values of both sample and standard solutions were kept below 0.1 to minimize the re-absorption effects at the excitation wavelength.

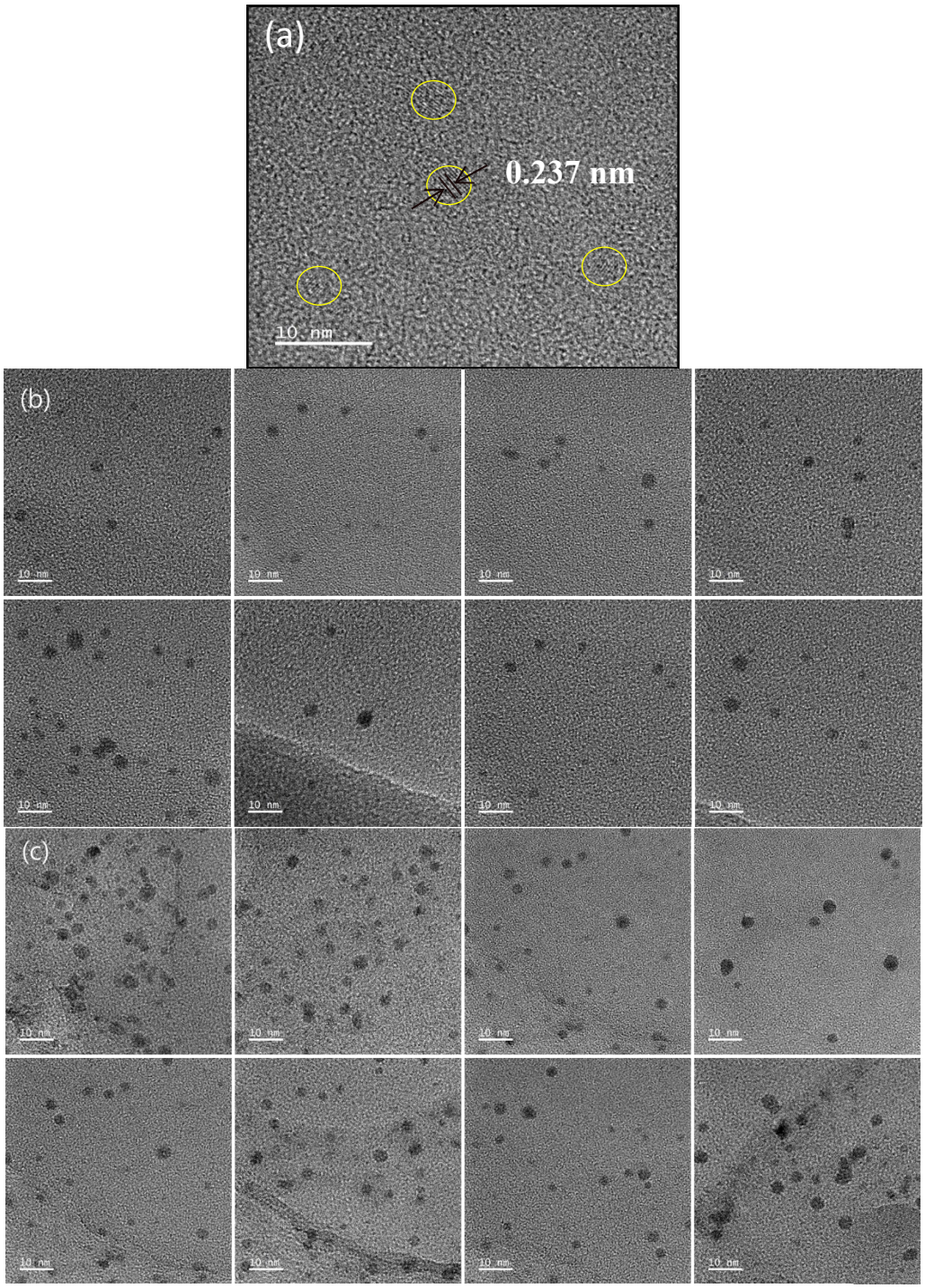

Fig. S1 (a) HRTEM image showing the crystalline lattice of AuNCs. Several images of numerous clusters (b) before and (c) after adding mercury ion for analyzing a size-distribution histogram. Scale bar is corresponding to 10 nm.

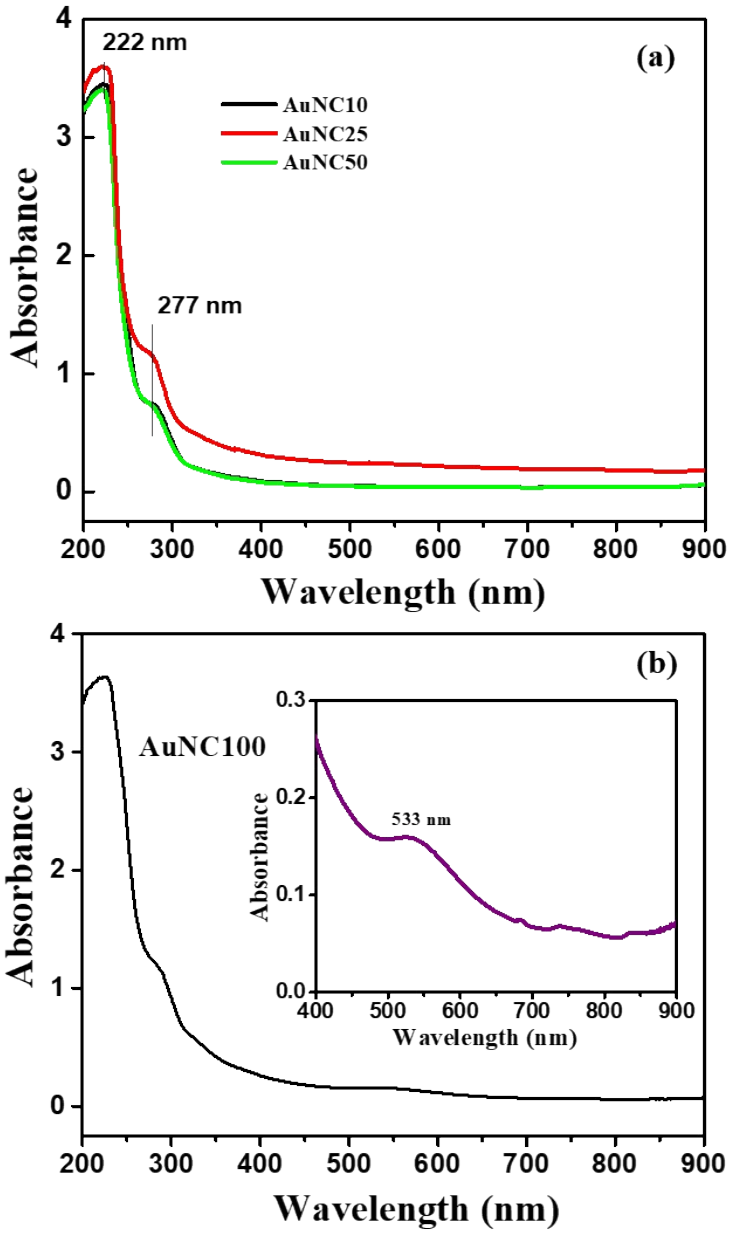

Fig. S2 (a, b) UV-vis absorption spectra for AuNCs synthesized using different NaOH concentrations as indicated (mM). [Inset of b: Surface plasmon peak for AuNPs].

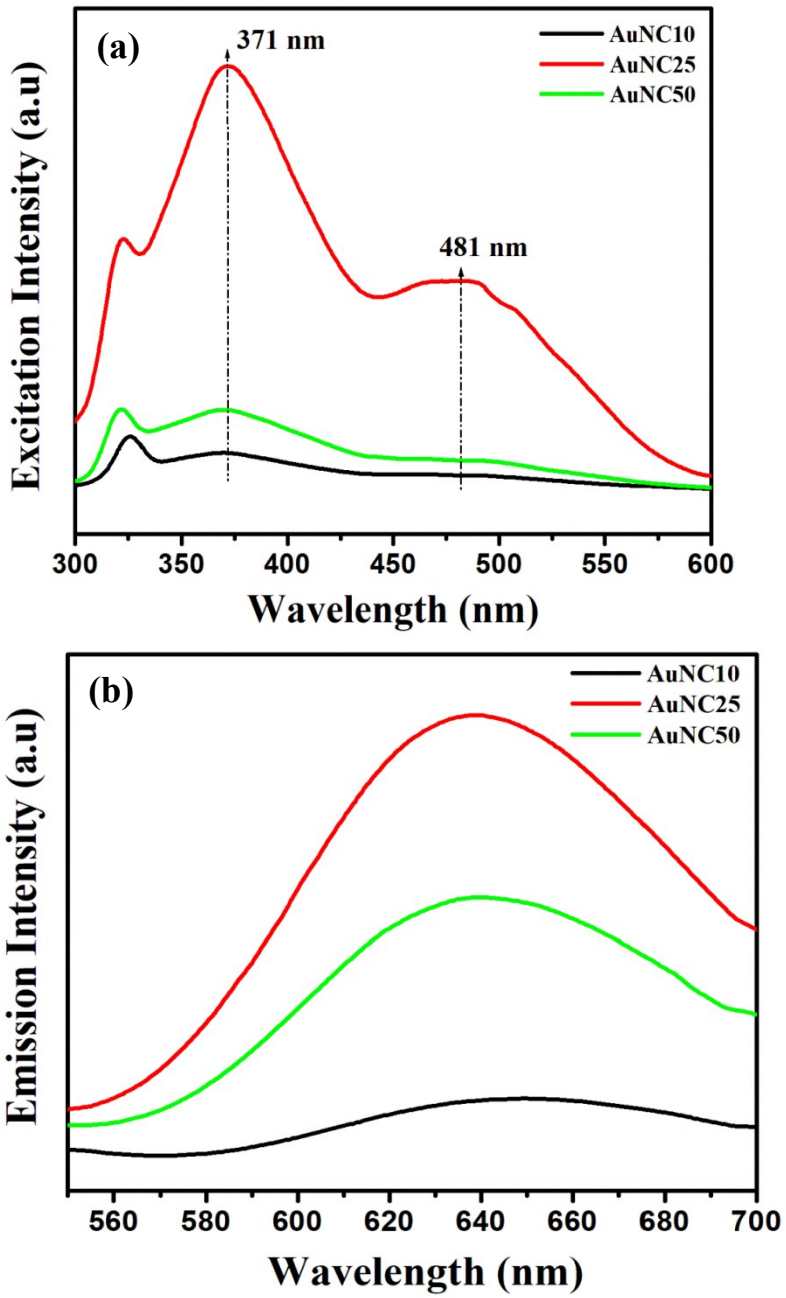

Fig. S3 (a) PLE and (b) PL spectra for synthesized AuNCs.

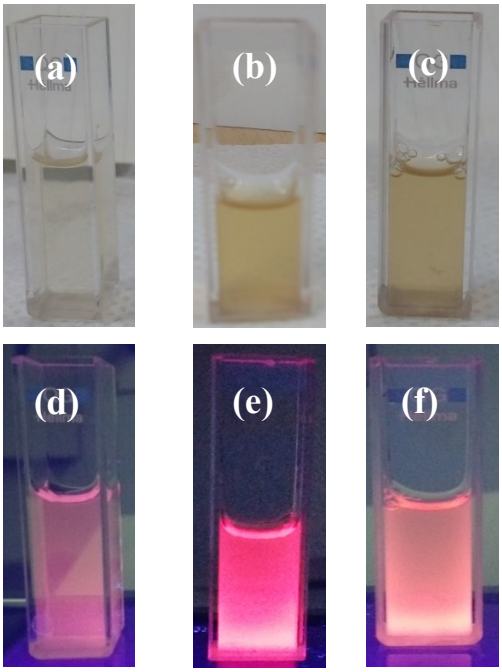

Fig. S4 Optical images under visible (a-c) and UV light illumination for AuNC10, AuNC25 and AuNC50 respectively.

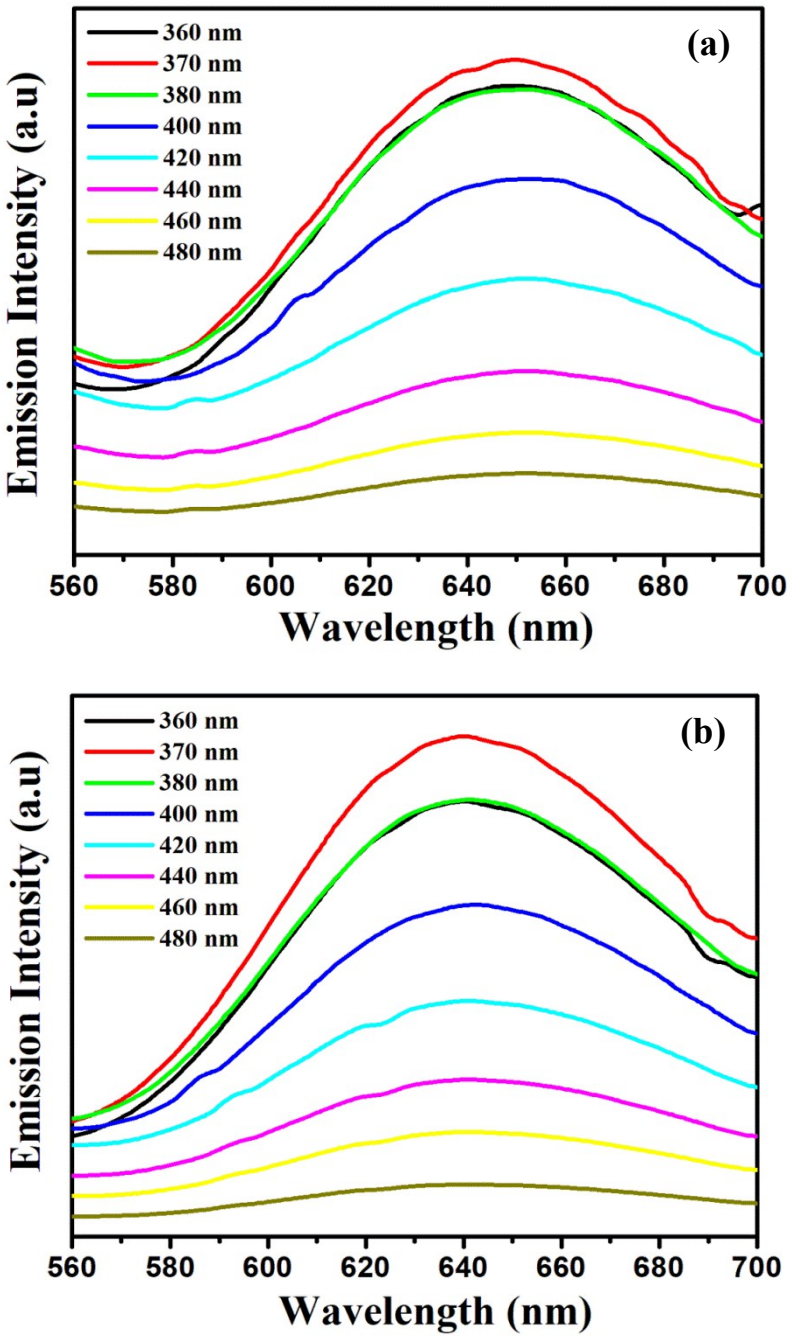

Fig. S5 Excitation wavelength dependent PL spectra for (a) AuNC10 and (b) AuNC50.

Table S1: Quantum yield values of synthesized AuNCs.

Sample	Absorbance	Integrated Area	Quantum Yield (%)
R6G	0.0736	31501.26876	94
AuNC10	0.0584	431.64049	1.55
AuNC25	0.0572	2449.10587	9.02
AuNC50	0.0605	1225.9003	4.26

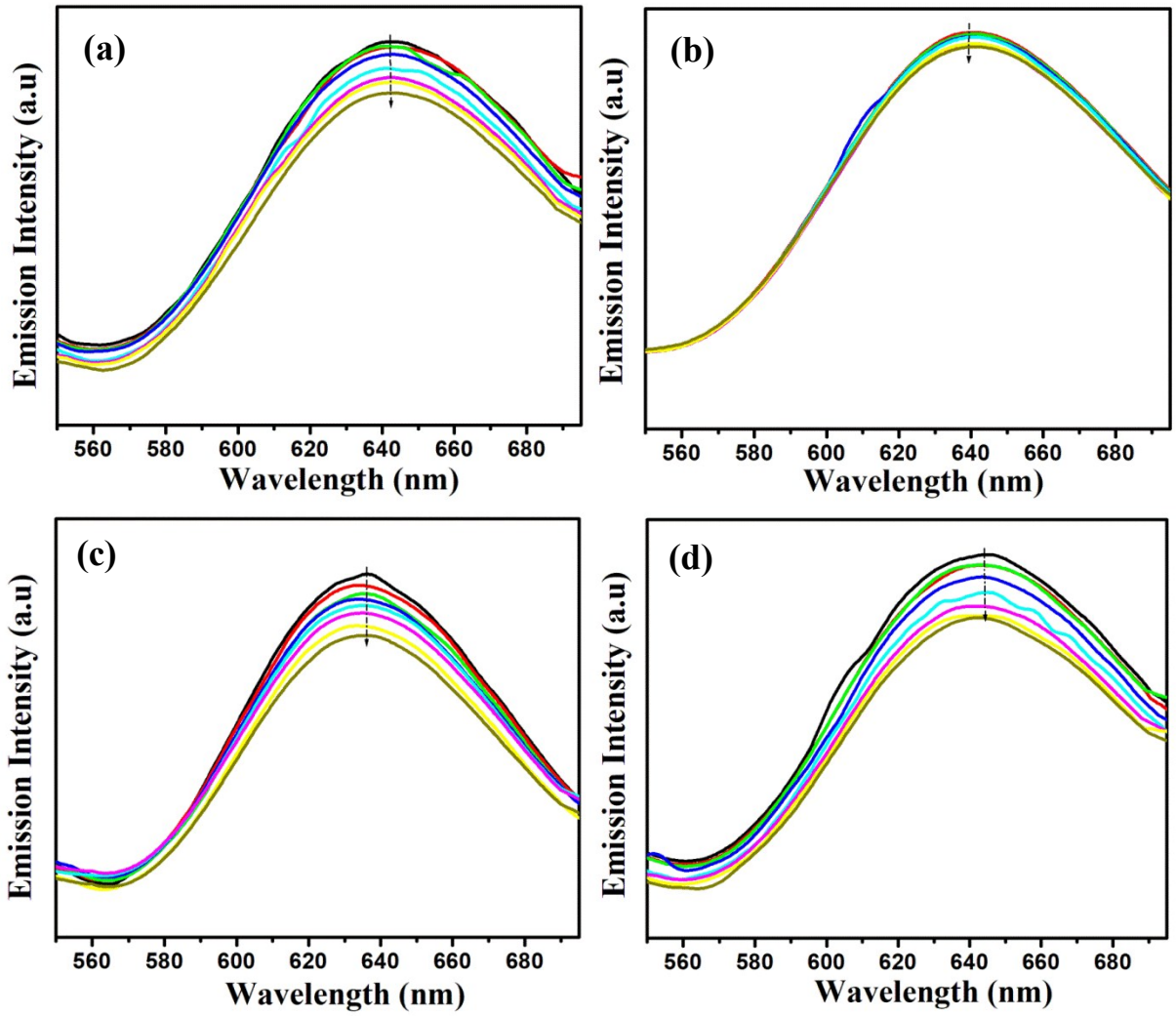

Fig. S6 Fluorescence profile of AuNCs with addition of different concentrations from 10 to 80 mM. (a) Na^{+}, (b) K^{+}, (c) Mg^{2+} and (d) Al^{3+}.

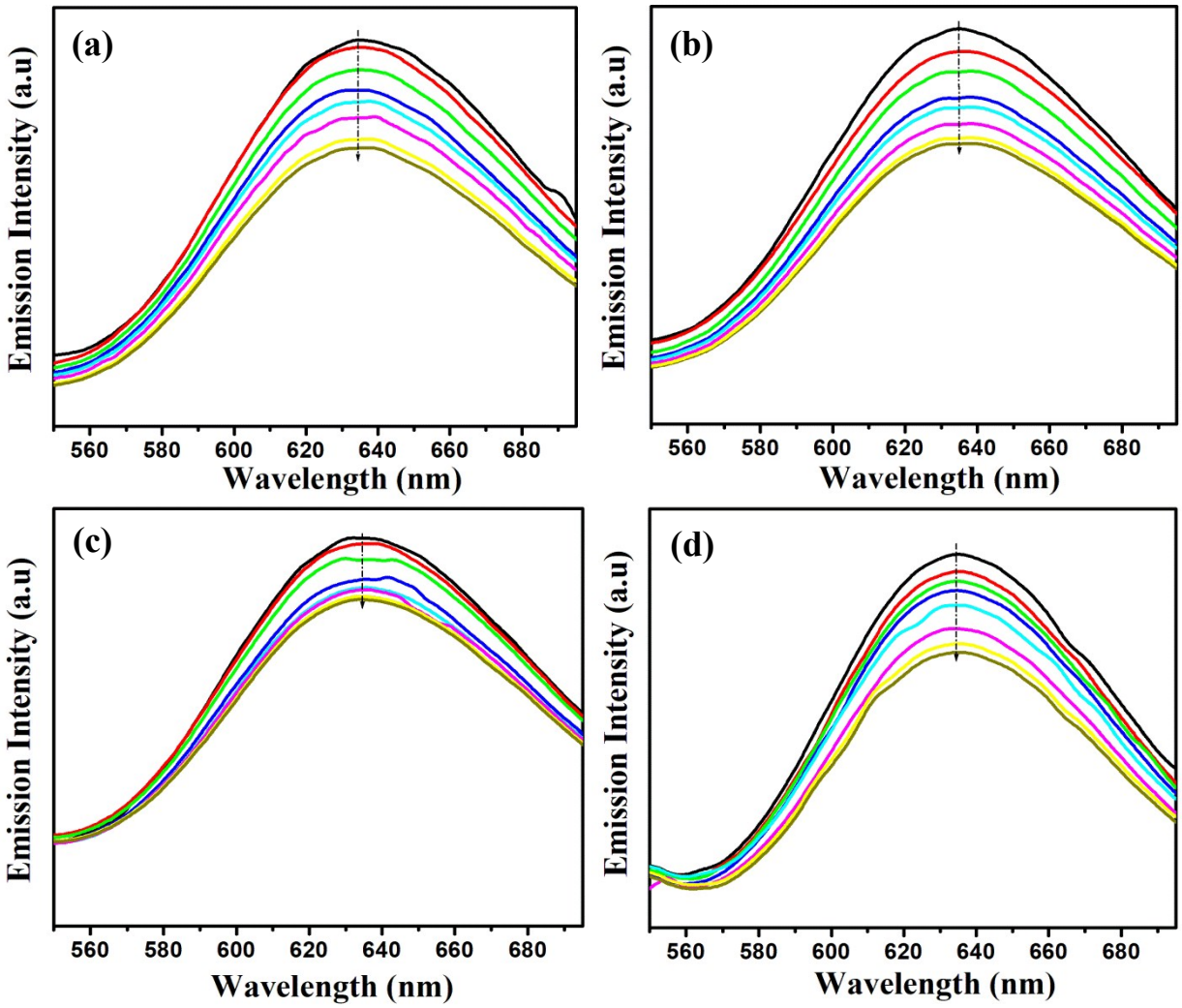

Fig. S7 Fluorescence profile of AuNCs with addition of different concentrations from 10 to 80 mM. (a) Ni^{2+}, (b) Co^{2+}, (c) Cu^{2+} and (d) Zn^{2+}.

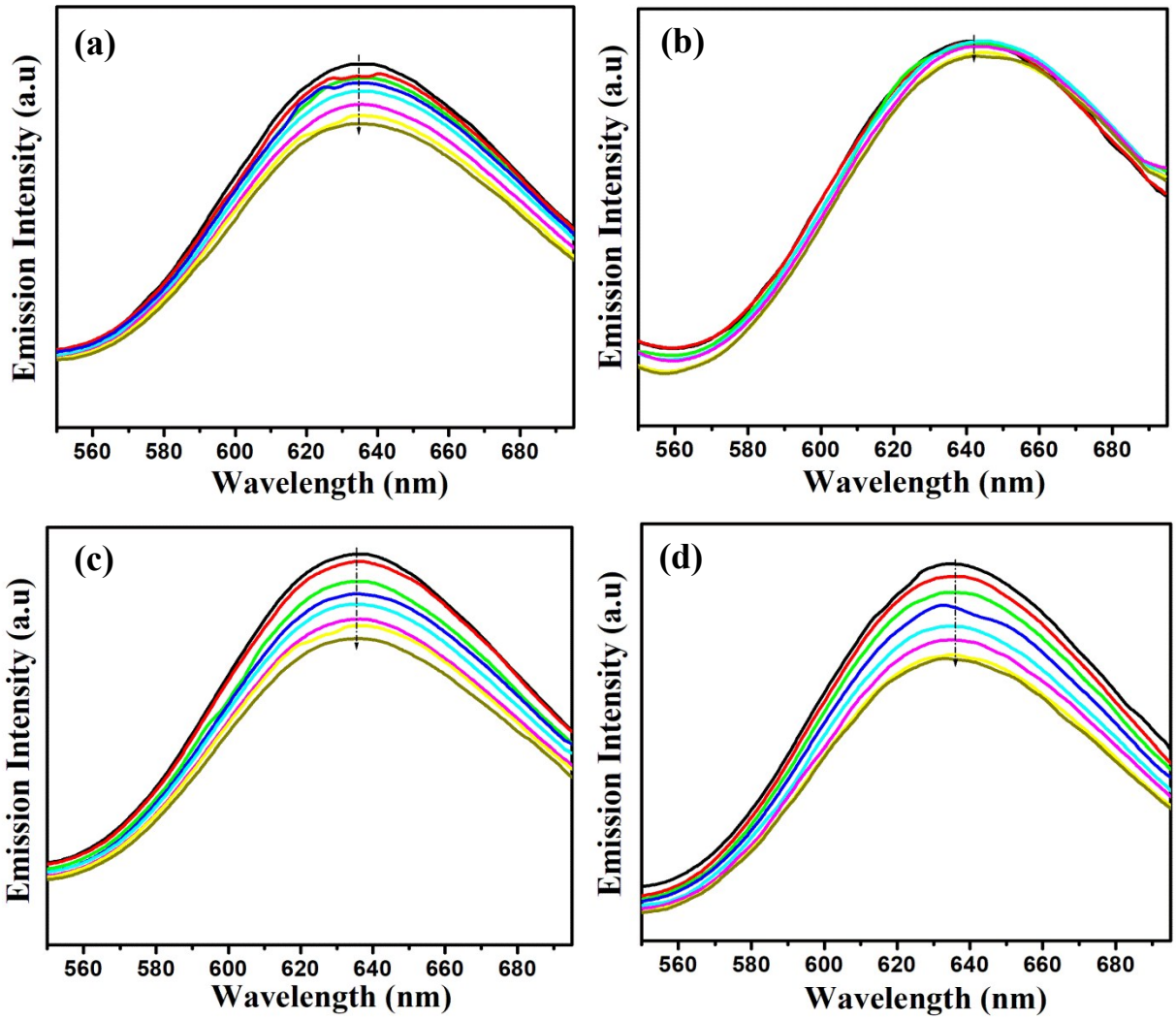

Fig. S8 Fluorescence profile of AuNCs with addition of different concentrations from 10 to 80 mM. (a) Mn^{2+}, (b) Pb^{2+}, (c) Fe^{2+} and (d) Fe^{3+}.

Table S2: Comparison of fluorescent based sensor for the detection of Hg^{2+}.

References	Synthesized Systems	Linear Range	LOD
4	AuNPs Capped with 3-MPA and AMP	0.5-3.5 μM	50 nM
5	DNA AuNP	96 nM-6.4 μM	40 nM
6	BSA-AuNCs	0.4-43.2 μM	80 nM
7	Fluorescent Carbon Nanoparticles	0-5 μM	10 nM
8	Trypsin AuNCs	50-600 nM	50 ± 10 nM
9	AIE organic NPs and AuNCs	50-600 nM	22.7 nM
10	Dye-Adsorbed AuNPs	0.01-10 μM	57 nM
This Study	Red emissive AuNCs	5-30 and 48-66 nM	6.99 nM

References:

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