

## Supporting Information

### Surface Motifs Regulated Aggregation Induced Emission in Gold-Silver Nanoclusters

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## **Experimental Section**

### **Chemicals and methods:**

**Chemicals:** Tetrachloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), silver nitrate ( $\text{AgNO}_3$ ), N-(2-Mercaptopropionyl)glycine, glutathione reduced (GSH), were purchased from Sigma-Aldrich. Other chemicals such as sodium borohydride ( $\text{NaBH}_4$ ), sodium hydroxide granules ( $\text{NaOH}$ ), methanol, and ethanol were purchased from Merck. High purity water ( $\sim 18.2 \text{ M}\Omega$ ) was used throughout the experiment. All the chemicals of highest purity grade were used without further purification.

### **Methods:**

#### **Synthesis of mono-metallic and bi-metallic nanoclusters:**

Luminescent gold and gold-silver alloy nanoclusters were synthesized by two step synthesis. In the first, polydisperse non luminescent Au nanoclusters were synthesized using N-(2-mercaptpropionyl)glycine (MPGH) as capping agent. Then, glutathione (GSH) assisted ligand exchange process was employed to prepare fluorescent Au and AuAg alloy cluster.

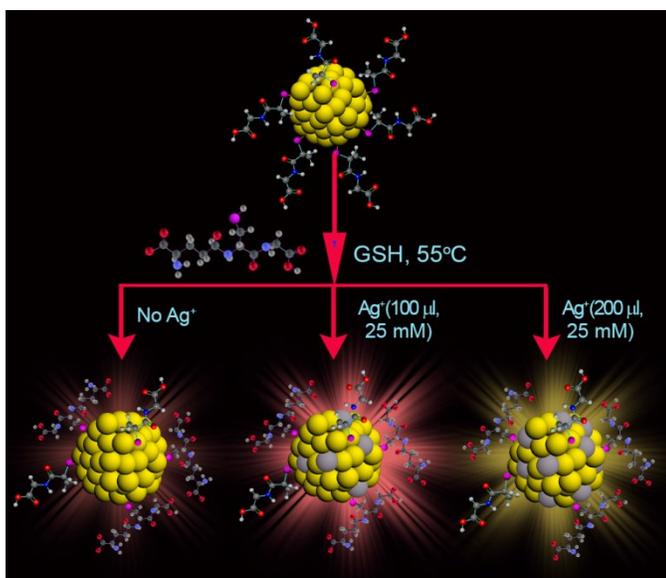
#### **MPG-protected non luminescent Au NCs:**

In a typical synthesis, 4 mL of 25mM  $\text{HAuCl}_3 \cdot 3\text{H}_2\text{O}$  was added to a 100 mL MeOH in 200 mL conical flask at  $0^\circ\text{C}$  (ice bath). Then, 160 mg of MPGH ligand was added to the reaction mixture and the reaction was allowed to stirrer for 30 minutes. After that, freshly prepared ice cold  $\text{NaBH}_4$  (200 mg, in 20 mL water) was rapidly injected in to the reaction mixture under vigorous stirring, and a black particles were formed immediately. The reaction was further allowed to stirring for another 30 minutes for complete reduction. Finally, the black precipitate was collected by centrifugation at 10000 rpm for 10 minutes. The particles washed at least two times with methanol/water (3:1) mixture to remove the excess salts, precursor. Then, the particles was kept overnight at room temperature to obtain dry polydisperse nanoclusters. The as prepared non luminescent Au NCs were dissolved in water for further experiment.

#### **Glutathione directed synthesis of Au and AuAg alloy nanoclusters:**

Red emitting Au NCs were prepared from as-prepared polydisperse Au NCs; typically 1.25 mL MPG capped Au NCs added to 8.75 mL deionized water. Then excess glutathione (307 mg) was added to the reaction mixture and stirred at  $55^\circ\text{C}$ . The reaction was monitored using absorption and photoluminescence (PL) spectroscopy, the reaction is completed within 18 hours. The as-prepared Au NCs emits red color under the exposures of UV lamp (365 nm). For bi-metallic AuAg

NCs synthesis different amount of  $\text{AgNO}_3$  (25 mM) was added during the ligand exchange process. The emission maxima of AuAg NCs are changed with varying the concentration of  $\text{Ag}^+$  ion. Typically, strong red emitting NCs (r-AuAg) is obtained when 100  $\mu\text{L}$   $\text{Ag}^+$  was added and yellow emitting NCs (y-AuAg) was obtained upon addition of 200  $\mu\text{L}$  of  $\text{Ag}^+$ . The synthesis scheme of mono-metallic Au NCs and bi-metallic AuAg NCs is illustrated in scheme 1.



**Scheme 1.** Schematic representation of the synthesis of Au and AuAg nanoclusters with tunable emission

### Instrumentation

The optical absorption spectra were taken with a UV-vis spectrophotometer (Shimadzu) using a cuvette with a path length of 1 cm at room temperature. The PL spectra of all of the samples were taken with a Fluoro Max-P (HORIBA JobinYvon) luminescence spectrophotometer. The transmission electron microscopy (TEM) was performed on a JEOL-JEM-2100F transmission electron microscopy system at an accelerating voltage of 200 kV. The samples for TEM analysis were prepared by drop casting of NCs solution onto a copper grid covered by a carbon film. The X-ray photoelectron spectroscopy (XPS) (Omicron Nanotechnology instrument) study was carried out to determine the binding energy. Raman spectra were recorded by using Horiba JobinYvon, (T64000 model) instrument by exciting the samples at 632 nm laser beam. Fourier-transform infrared (FTIR) spectroscopy analyses were performed on a SHIMADZU made FTIR-8300

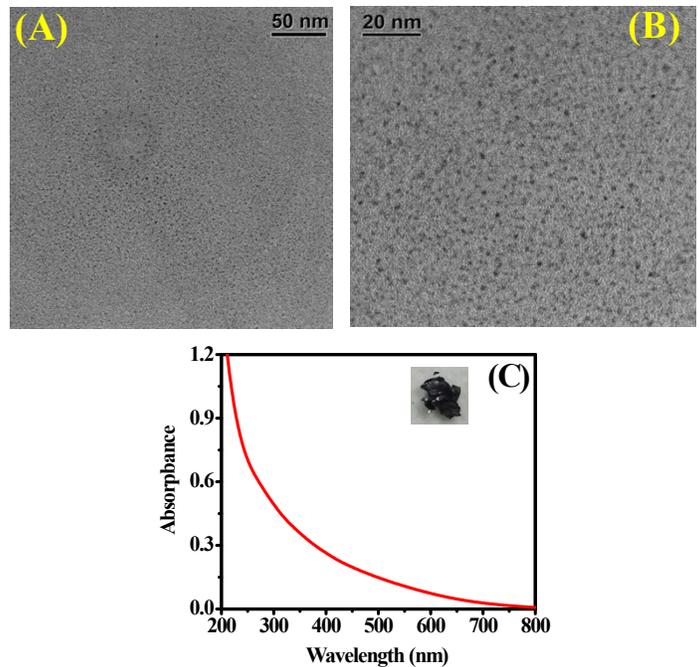
spectrometer using KBr pellets. The zeta potential and dynamic light scattering (DLS) sizes were measured with a Malveron Zetasizer instrument. For the time correlated single photon counting (TCSPC) analysis, the samples were excited at 415 nm using a Spectra LED light source for the measurement of phosphorescence lifetimes. The typical full width at half-maximum (FWHM) of the system response using a liquid scatter was about 90 ps. The fluorescence decays were collected on a Hamamatsu MCP photomultiplier. Equation (1) is used to analyze the experimental time-resolved fluorescence decays,  $P(t)$ :

$$P(t) = b + \sum_i^n \alpha_i \exp(-t/\tau_i) \quad (1)$$

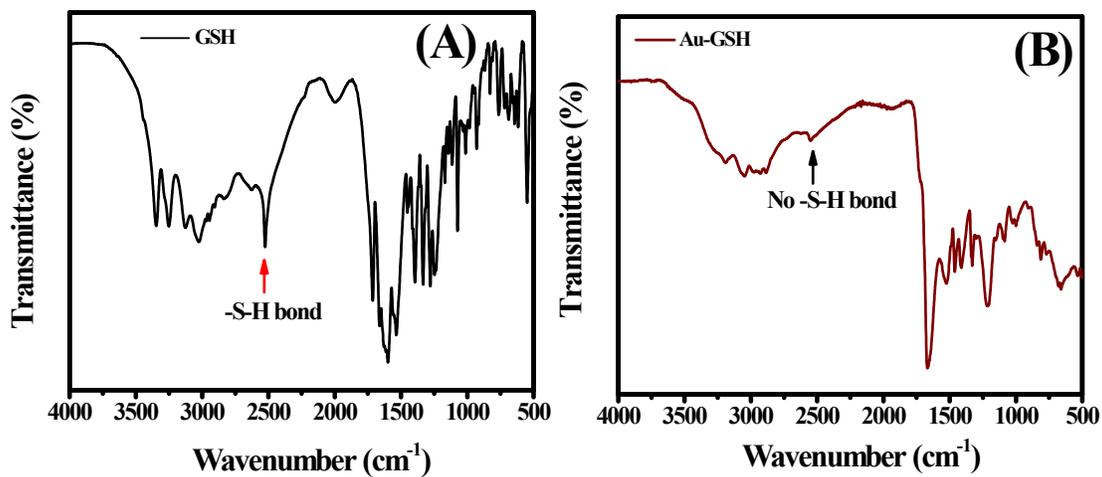
Here,  $n$  is the number of emissive species,  $b$  is the baseline correction (“DC” offset), and  $\alpha_i$  and  $\tau_i$  are, respectively, the pre-exponential factor and the excited-state fluorescence decay time associated with the  $i^{\text{th}}$  component. The average decay time,  $\langle \tau \rangle$ , is calculated from following equation.<sup>24</sup>

$$\langle \tau \rangle = \sum_{i=1}^n \beta_i \tau_i \quad (2)$$

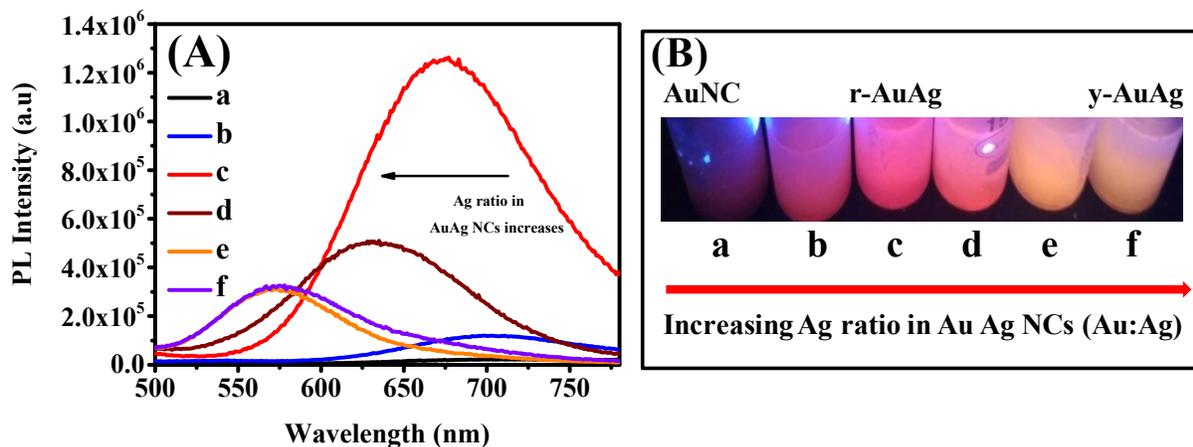
Where  $\beta_i = \alpha_i / \sum \alpha_i$  and  $\beta_i$  is contribution of the decay component.



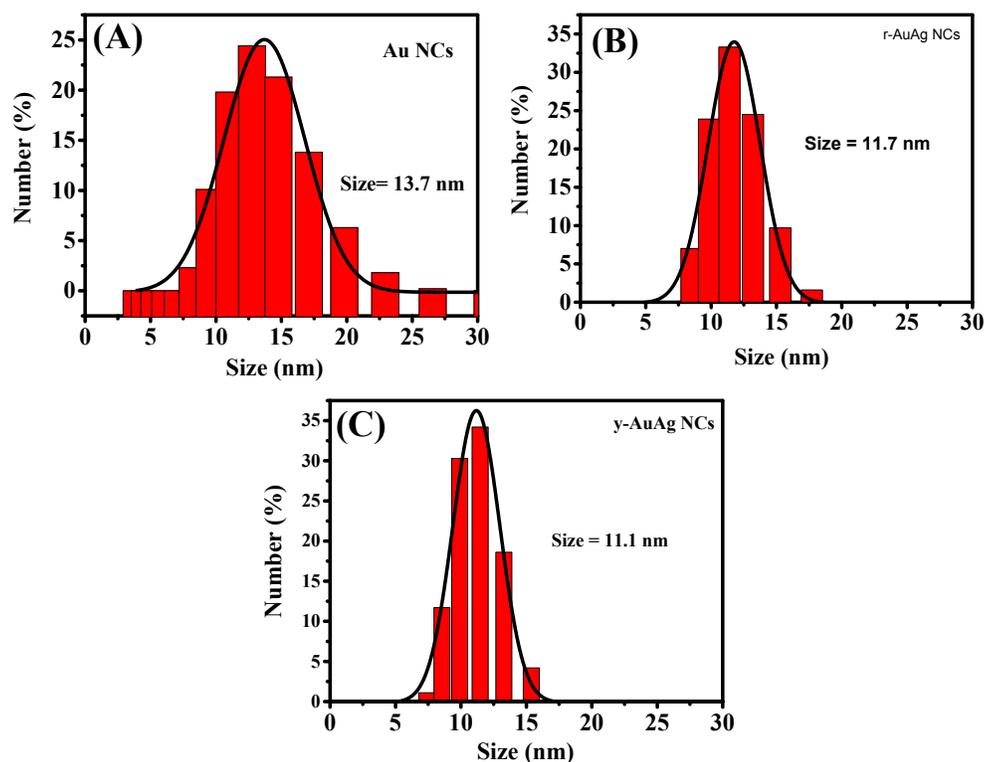
**Fig. S1.** TEM images of MPG-capped Au NCs with scale bar (A) 50 nm, (B) 20 nm and (C) absorption spectra Au NCs and inset shows the digital picture of NCs powder.



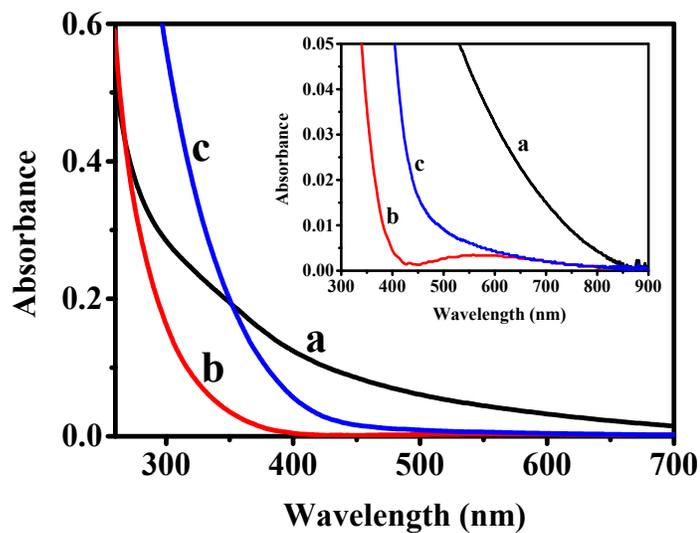
**Fig. S2.** FTIR spectrum of (A) glutathione (GSH), and (B) bimetallic AuAg NCs capped by GSH.



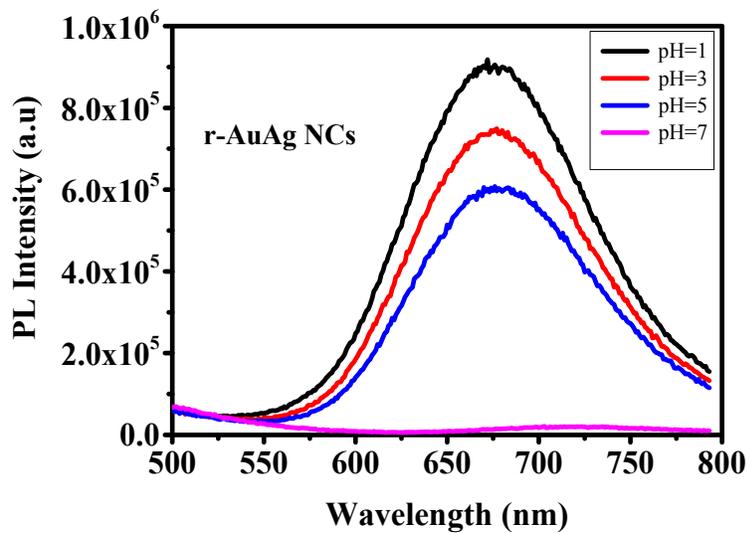
**Fig. S3.** (A) Tuning of emission wavelength of Au NCs with different Au/Ag molar ratio (a) 1:0, (b) 1:0.14, (c) 1:0.71, (d) 1:0.98, (e) 1:1.36 and (d) 1:1.51 and (B) Digital picture of corresponding NCs under UV-light excitation (365 nm).



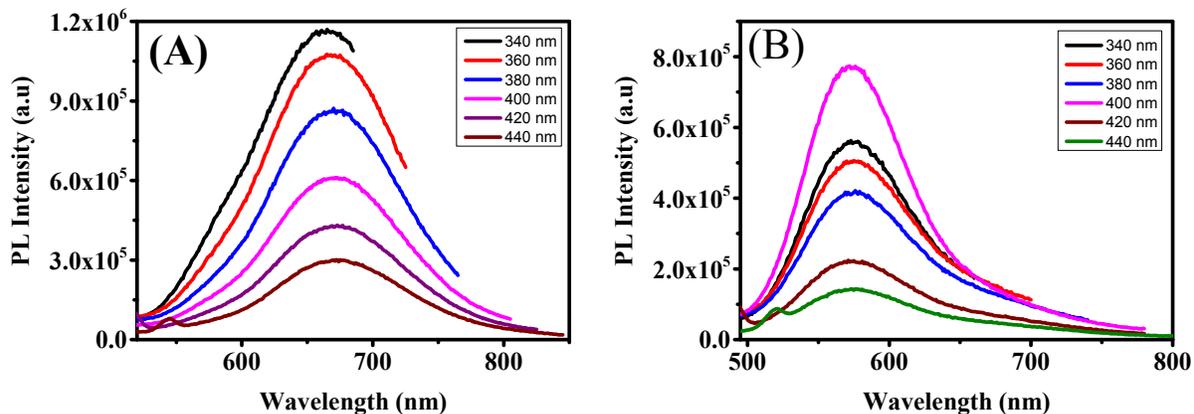
**Fig. S4.** DLS size distribution plot of (A) Au NCs, (B) r-AuAg NCs and (C) y-AuAg NCs.



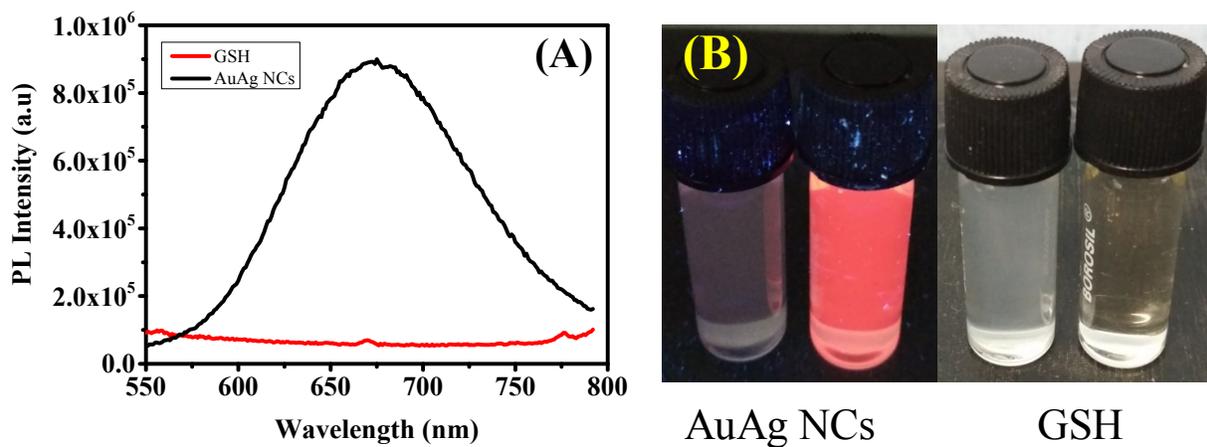
**Fig. S5.** Absorption spectra of (a) Au NCs, (b) r-AuAg NCs and (c) y-AuAg NCs and inset shows the zoomed view.



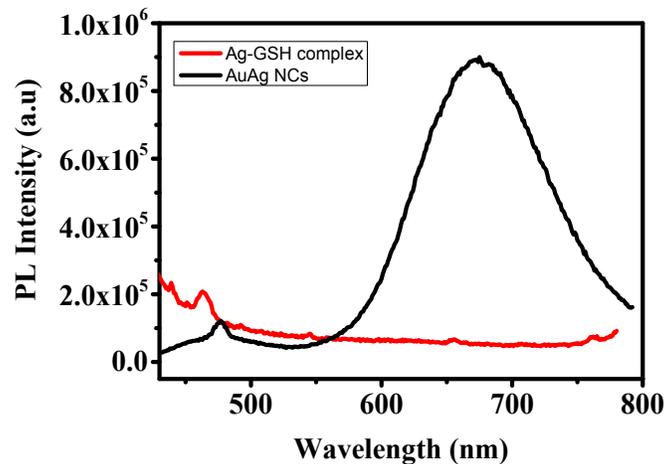
**Fig. S6.** PL spectra of r-AuAg NCs at different pHs under 400 nm excitation wavelength.



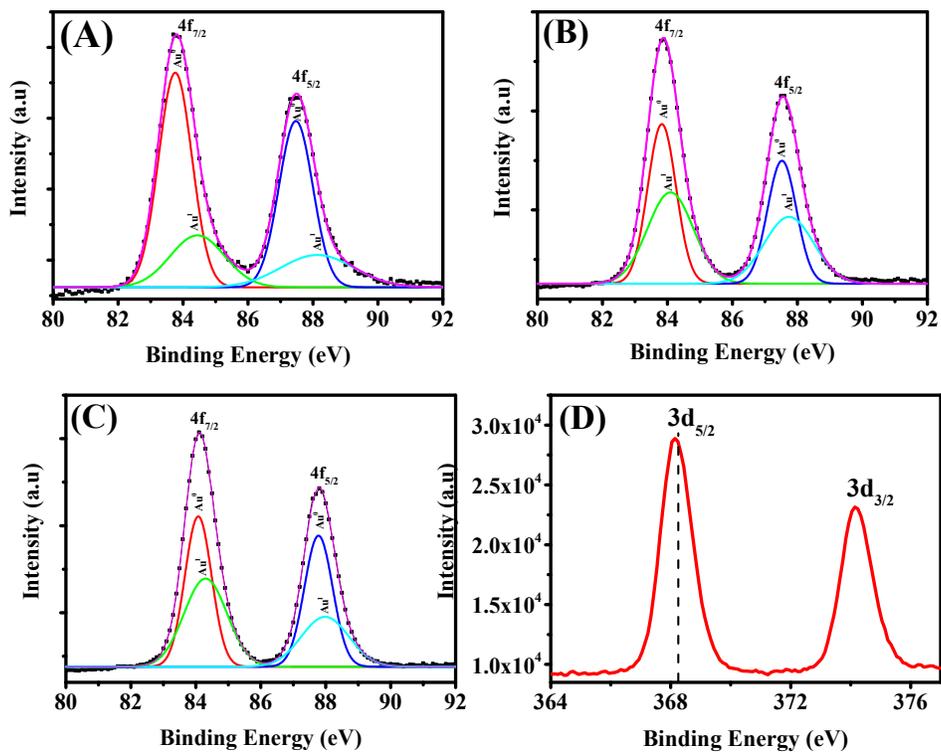
**Fig.S7.** Excitation wavelength dependent emission spectra of (A) r-AuAg NCs and (B) y-AuAg NCs



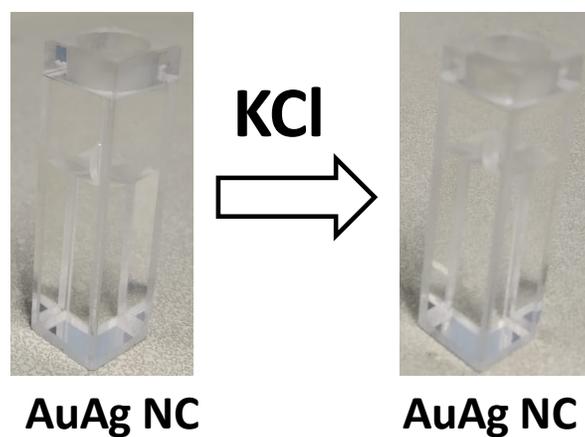
**Fig. S8.** Emission spectra of (A) AuAg NCs and control experiment without metal precursor, and (B) digital picture of control reaction and AuAg NCs under UV-light excitation (365 nm)



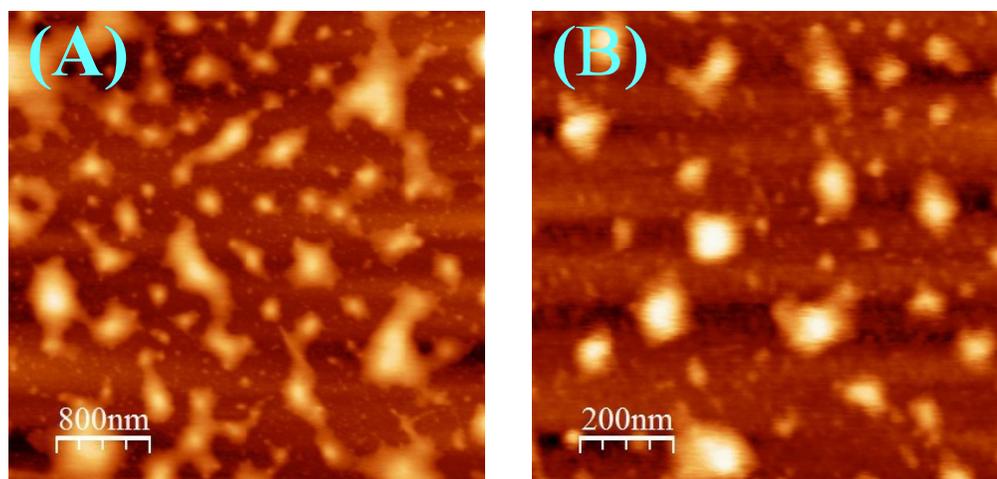
**Fig. 9.** Emission spectra of AuAg NCs and Ag-GSH complex.



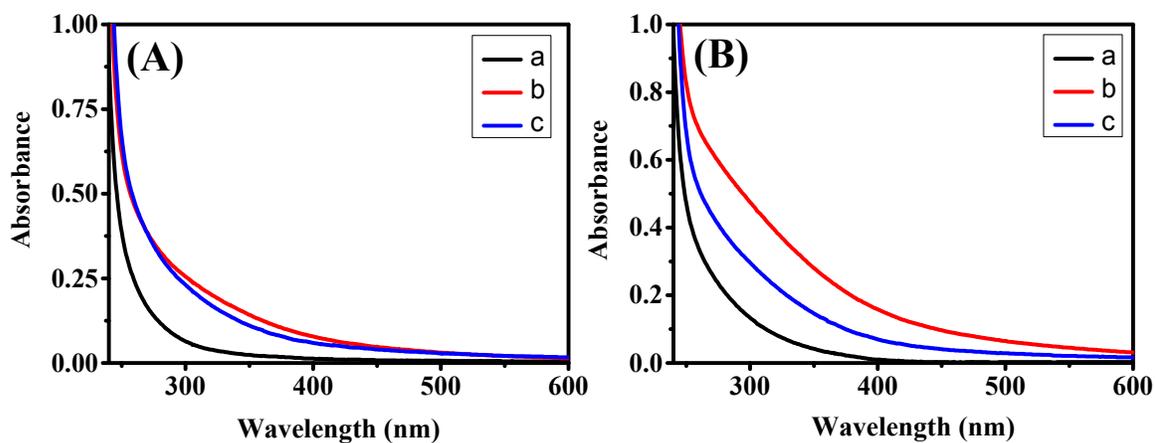
**Fig. S10.** X-ray photoelectron spectra of Au-4f of (A) Au NCs, (B) r-AuAg NCs and (C) y-AuAg NC. (D) XPS spectrum of Ag-3d in y-AuAg NCs, dotted line indicates position of Ag(0).



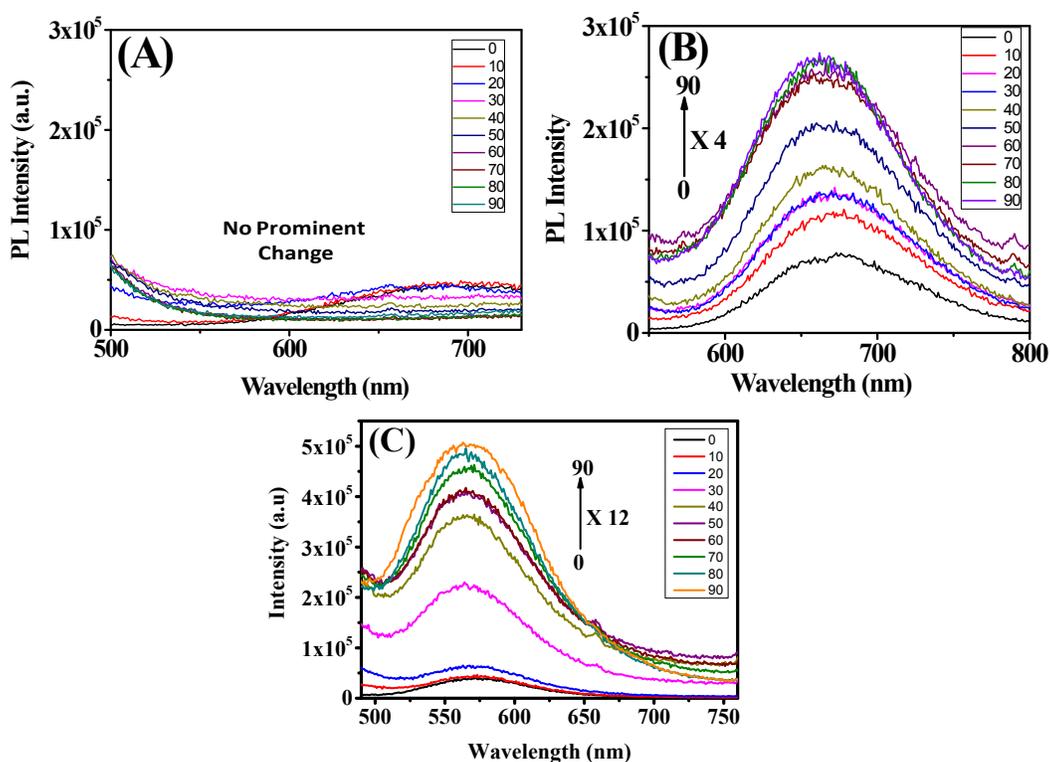
**Fig. S11.** No  $\text{Ag}^+$  ion is present in AuAg NCs as there is no precipitation of AgCl after addition of KCl solution.



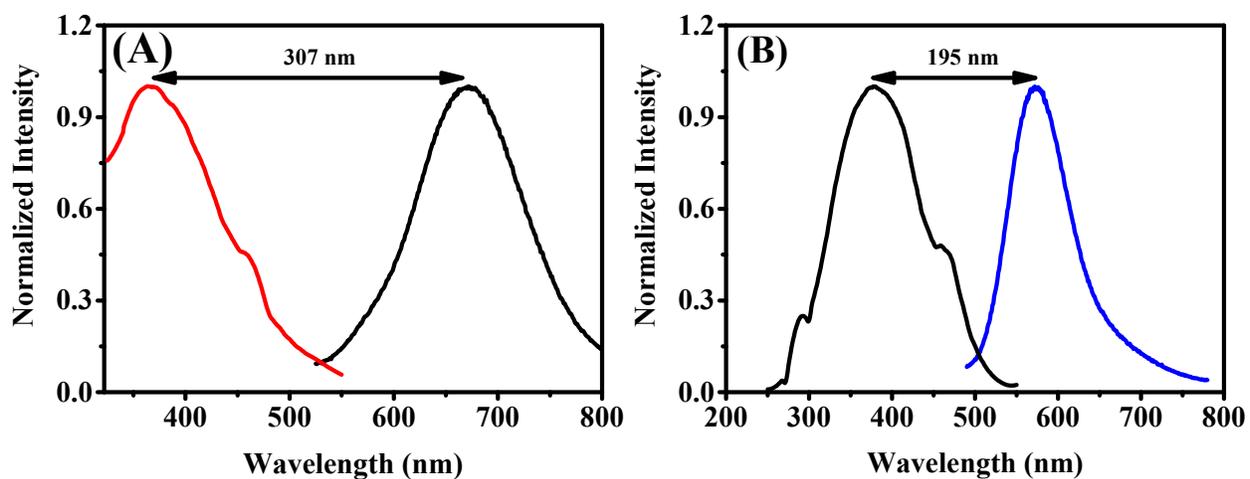
**Fig. S12.** AFM images of (A) r-AuAg NCs and (B) y-AuAg NCs



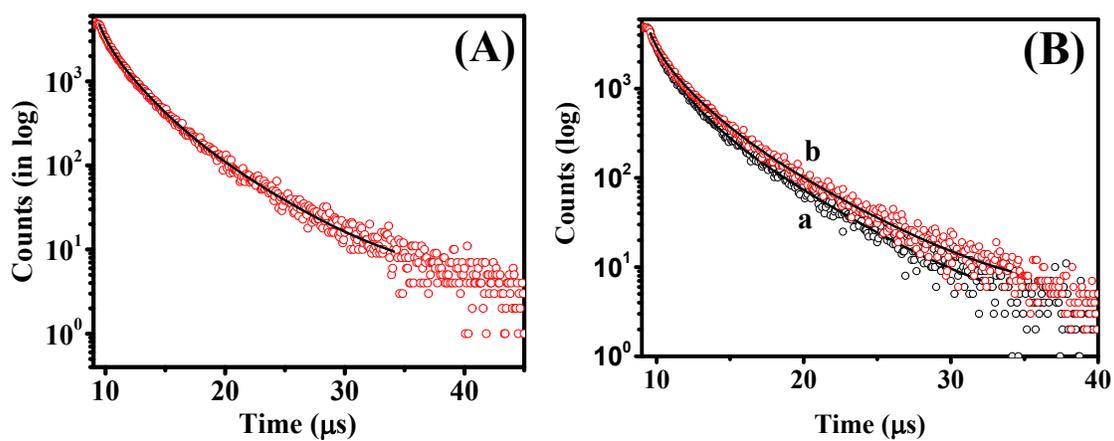
**Fig. S13.** UV-Vis absorption spectra of (A) r-AuAg and (B) y-AuAg NC with (a)  $f_v=0\%$ , (b)  $f_v=60\%$  and (c)  $f_v=90\%$  ethanol/water mixture.



**Fig. S14.** PL spectra of (A) Au NCs, (B) r-AuAg NCs and (C) y-AuAg NCs in water-EtOH mixture with volume fraction ( $f_v$ ) = 0-90%.



**Fig. S15.** Stokes shift of (A) r-AuAg NCs and (B) y-AuAg, respectively.



**Fig. S16.** Time resolved decay curves of (A) Au NCs and (B) r-AuAg NCs (a)  $f_v=0\%$  and (b)  $f_v=60\%$  ethanol ( $\lambda_{ex}=415$  nm).

**Table 1:** Time-resolved fluorescence data of Au NCs, AuAg NCs at different emission wavelengths

Systems	Excitation (Wavelength)	Emission (Wavelength)	$\tau_1$ ( $\mu\text{s}$ )	$\tau_2$ ( $\mu\text{s}$ )	$\tau_3$ ( $\mu\text{s}$ )	$\langle\tau\rangle$ ( $\mu\text{s}$ )
Au NCs	400	735	1.34 (0.52)	2.69 (0.32)	5.39 (0.16)	2.42
Red-AuAg NCs	400	674	1.23 (0.48)	2.47 (0.36)	4.95 (0.16)	2.27
Red-AuAg NCs (in 60% Ethanol)	400	620	1.36 (0.48)	2.78 (0.33)	5.57 (0.19)	2.62
Yellow-AuAg NCs	400	574	0.53 (0.60)	2.14 (0.40)	-----	1.17
Yellow-AuAg NCs (in 60% Ethanol)	400	564	1.15 (0.55)	2.31 (0.10)	4.62 (0.35)	2.48