Supporting Information

Highly luminescent Ag^+ nanoclusters for Hg^{2+} ion detection

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S1. Experimental

1. Materials

Ultrapure Millipore water (18.2 MΩ) was used as an universal solvent unless indicated otherwise. All glassware was washed with *aqua regia*, and rinsed with ethanol and ultrapure water. Sodium borohydride ($NaBH_4$), L-glutathione reduced (GSH), cetyltrimethyl ammonium bromide (CTAB), decanoic acid (DA), tetramethylammonium hydroxide pentahydrate (TMAH), metal salts and anions from Sigma-Aldrich; sodium chloride, sodium hydroxide (NaOH), silver nitrate ($AgNO_3$), ethanol, and methanol from Merck; toluene from Tedia; chloroform from Fisher; were used as received.

2. Instruments

Luminescence and UV-vis spectra were recorded on a PerkinElmer LS55 fluorescence spectrometer and a Shimadzu UV-1800 spectrometer, respectively. The molecular weight of b-Ag NCs and Hg^{2+}−Ag NCs were analyzed by matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) and electrospray ionization (ESI) mass spectrometry on a Bruker Daltonics Autoflex II TOF/TOF system and a Bruker microTOF-Q system, respectively. The MALDI samples were prepared by mixing 1 μL of the as-synthesized Ag NCs or Hg^{2+}−Ag NCs in aqueous solution with 1 μL of saturated α-cyano-4-hydroxycinnamic acid (CHCA) solution. The saturated CHCA solution was prepared by dissolving 20 mg of CHCA in 0.999 mL of ethanol, followed by the addition of 1 μL of trifluoroacetic acid. X-ray photoelectron spectroscopy (XPS) was carried out on a VG ESCALAB MKII spectrometer. Narrow-scan XPS spectra of Ag 3d core levels were deconvoluted by the XPSPEAK software (Version 4.1), using adventitious carbon to calibrate the binding energy of C 1s as 284.5 eV. Transmission electron microscopy (TEM) images were taken on a JEOL JEM 2010 microscope operating at 200 kV.

3. Synthesis of the b-Ag NCs in Aqueous Solution

Synthesis of the b-Ag NCs in toluene. Aqueous solutions of $AgNO_3$ (20 mM) and GSH (50 mM) were prepared with ultrapure water. An aqueous solution of $NaBH_4$ (112 mM) was freshly prepared by dissolving 43 mg of $NaBH_4$ in 8 mL of ultrapure water, followed by the addition of 2 mL of 1 M NaOH solution. The addition of a controlled quantity of NaOH to the $NaBH_4$ solution was used to improve the stability of the borohydride ions against hydrolysis. In a typical synthesis of GSH-Ag NCs in aqueous solution, GSH solution (150 μL, 50 mM), $NaBH_4$ solution (50 μL, 112 mM), and $AgNO_3$ solution (125 μL, 20 mM) were added sequentially to water (4.85 mL) under vigorous stirring. The GSH-Ag NCs in aqueous solution (5 mL) were collected after 10 min, followed by the addition of 5 mL of CTAB in ethanol (100 mM). The mixture was stirred for 20 seconds. Hydrophobic CTAB-protected GSH-Ag NCs were formed. Toluene (5 mL) was then added and stirred continuously for one more minute. The CTAB-protected GSH-Ag NCs were completely transferred to toluene within 5 min. The CTAB-protected GSH-Ag NCs in toluene were incubated at room temperature for 26 h. The aged toluene solution could then produce a strong blue emission under UV illumination.

Phase transfer of the b-Ag NCs from toluene to aqueous solution. Hydrophobic tetramethylammonium decanoate (TMAD) was used to transfer the b-Ag NCs back to the aqueous phase. Stock methanolic TMAD solution was prepared by dissolving DA (1.7 g) and TMAH (1.8 g) in 100 mL of methanol. In a typical phase transfer process, the b-Ag NCs in toluene (5 mL) were collected, followed by the sequential addition of chloroform (5 mL), water (5 mL), and TMAD (5 mL). The mixture was stirred for 1 min. The b-Ag NCs were then transferred back to the aqueous phase. The b-Au NCs were stored in the fridge (4 ^{o}C) without inert gas protection.

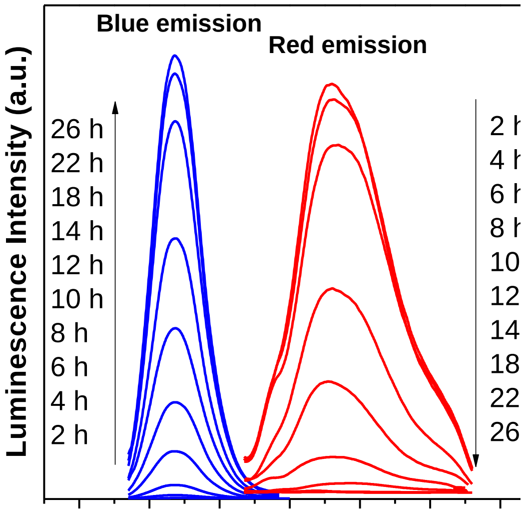

Fig. S1 Time-resolved evolution of photoemission spectra of the b-Ag NCs in toluene. The luminescence intensity at 435 nm (λ_{ex} = 350 nm) gradually increased with time from 2 to 26 h, which correlated well with the decrease of the 660 nm peak (λ_{ex} = 480 nm), therefore suggesting the transformation of r-Ag NCs to b-Ag NCs with time.

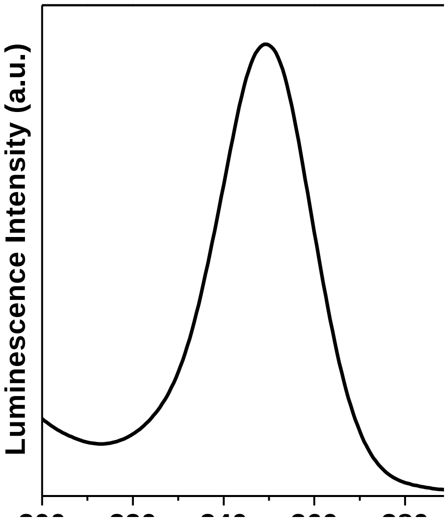

Fig. S2 Photoexcitation (λ_{em} = 435 nm) spetrum of the b-Ag NCs in toluene.

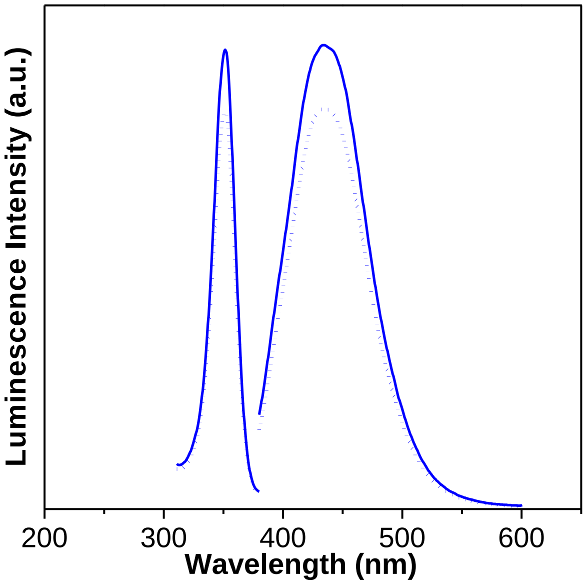

Fig. S3 Luminescence spectra (λ_{ex} = 350 nm) of the b-Ag NCs in aqueous solution at different temperatures: 4 ^{o}C (solid line) and 25 ^{o}C (dotted line).

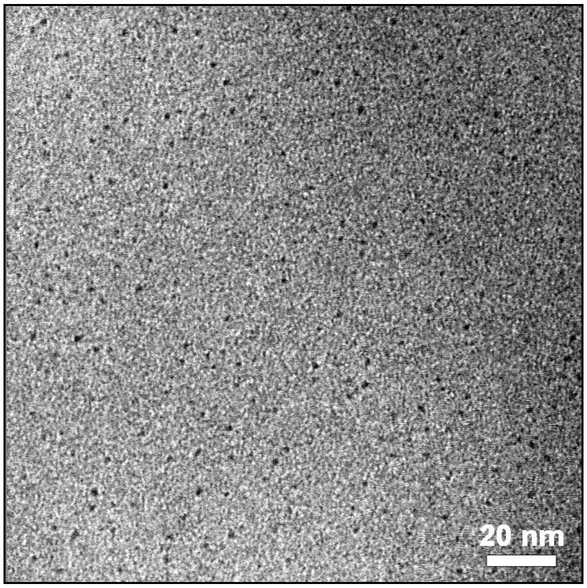

Fig. S4 Representative TEM image of the b-Ag NCs in toluene.

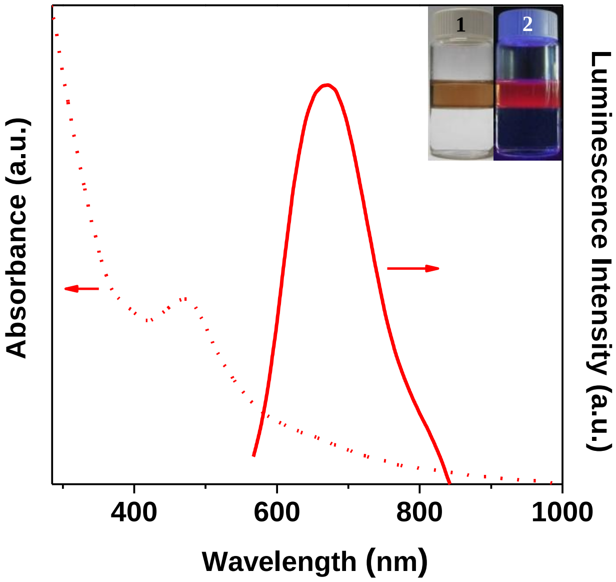

Fig. S5 Optical absorption (dotted line) and photoemission (solid line, $\lambda_{ex} = 480$ nm) spectra of the r-Ag NCs obtained by the redution of b-Ag NCs with $NaBH_4$ in toluene. The inset shows digital photos of the r-Ag NCs under visible (item 1) and UV (item 2) light.

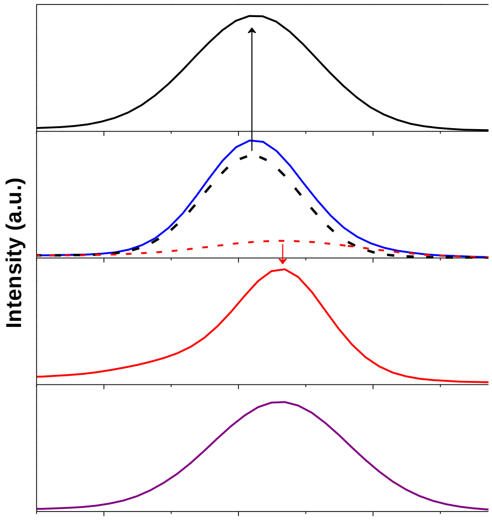

Fig. S6 XPS spectra of thiolate-Ag^+ complexes (black line), b-Ag NCs (blue line), large Ag nanoparticles (red line; > 3 nm, prepared by the reduction of $AgNO_3$ with $NaBH_4$ without the addition of protecting agents), and r-Ag NCs (purple line; prepared by the reduction of b-Ag NCs with $NaBH_4$).

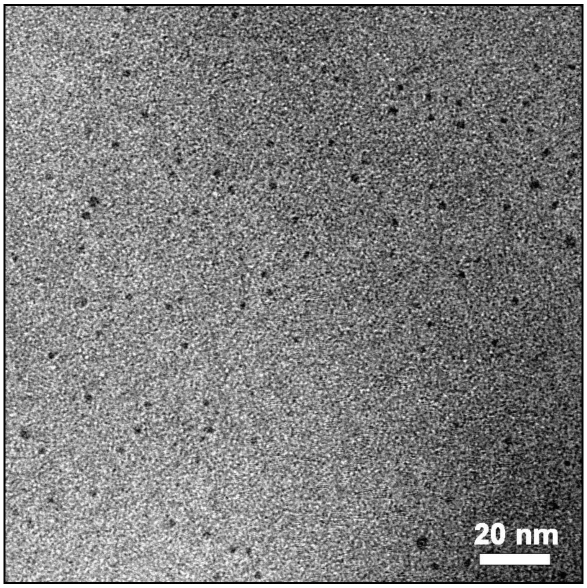

Fig. S7 Representative TEM image of the Hg^{2+}−Ag NCs.

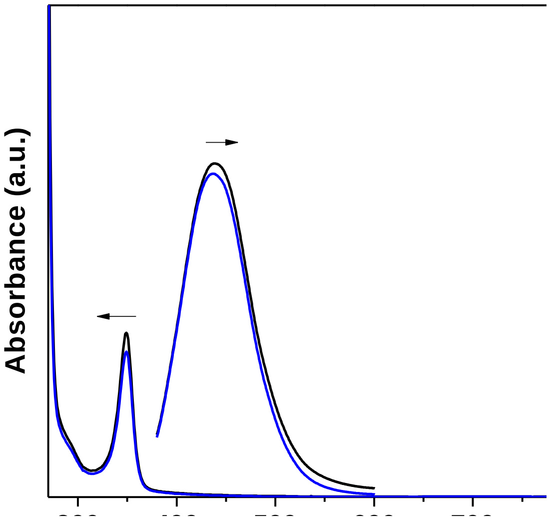

Fig. S8 Optical absorption and photoemission spectra (λ_{ex} = 350 nm) of the b-Ag NCs in aqueous solution freshly prepared (black lines) and after 6 months storage (blue lines) at room temperature without N_2 protection.

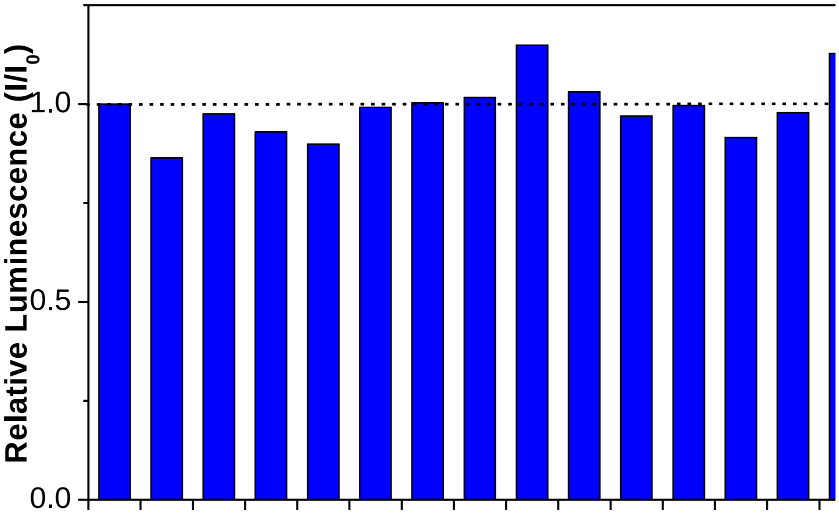

Fig. S9 Relative luminescence (*I/I$_0$*) at λ_{ex} = 350 nm of aqueous b-Ag NCs solutions (4.5 μM) in the presence of 250 μM of different metal ions.

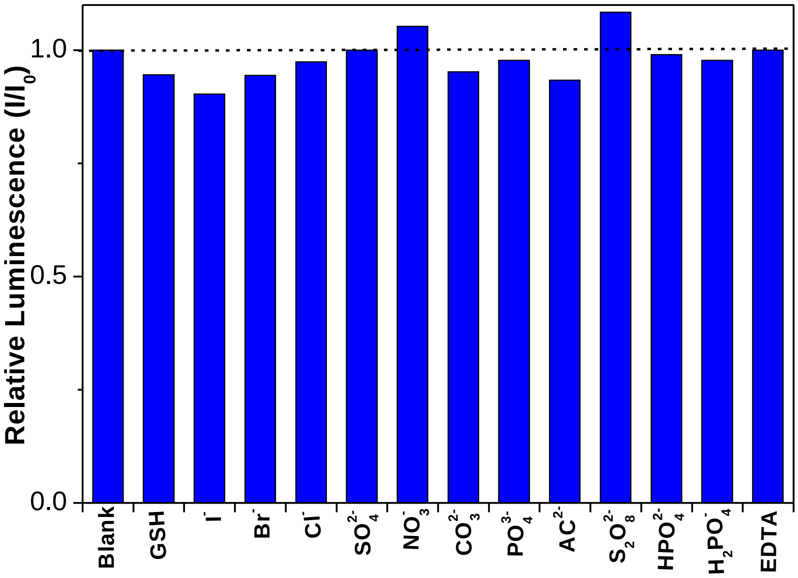

Fig. S10 Relative luminescence (*I/I$_0$*) at λ_{ex} = 350 nm of aqueous b-Ag NCs solutions (4.5 μM) in the presence of 250 μM of GSH and different anions.

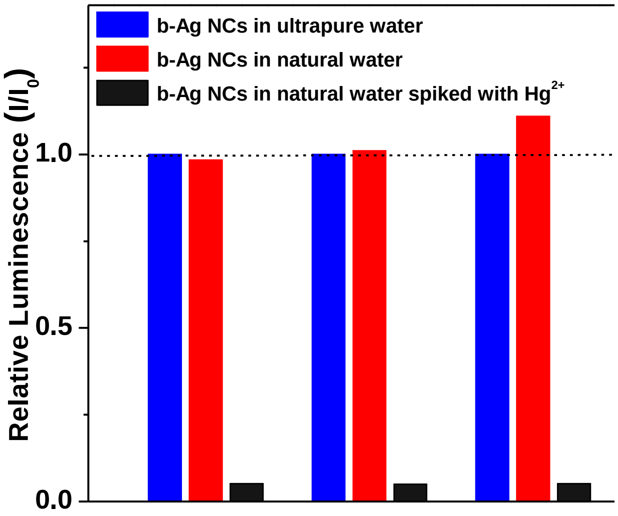

Fig. S11 Relative luminescence (*I*/*I*$_o$) at λ_{ex} = 350 nm of b-Ag NCs (4.5 μM) in different real water samples in the presence of Hg^{2+} ions (10 μM).

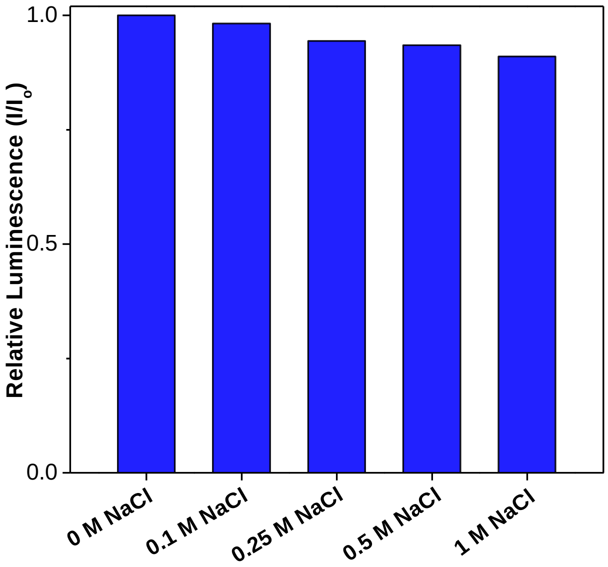

Fig. S12 Relative luminescence (*I*/*I*$_o$) at λ_{ex} = 350 nm of aqueous b-Ag NCs solutions (4.5 μM) in the presence of NaCl with different concentrations.