Supporting Information

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Near-infrared Electrochemiluminescence from Orange Fluorescent Au Nanoclusters in Water

Jun Myung Kim, Seonghyun Jeong, Jae Kyu Song,* and Joohoon Kim*

Department of Chemistry, Research Institute for Basic Sciences, KHU-KIST Department of
Converging Science and Technology, Kyung Hee University, Seoul 02447, Korea

***Corresponding Author: jkim94@khu.ac.kr**

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Experimental Section

Chemicals and materials Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), reduced L-glutathione (≥98%), sodium borohydride ($NaBH_4$, 99%), potassium nitrate (KNO_3, 99.999%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99.999%), trimethylamine (TMA, 45 wt.% in H_2O), triethylamine (TEA, ≥ 99%), tripropylamine (TPA, ≥ 98%), 2-(dimethylamino) ethanol (DMAE, ≥99.5%), 2-(diethylamino) ethanol (DEAE, ≥99.5%), 2-(dibutylamino) ethanol (DBAE, 99%), *N,N*-diethylethylenediamine (DEDA, ≥99%), hydrogen peroxide (H_2O_2, 30 wt.% in H_2O), and potassium peroxodisulfate ($K_2S_2O_8$, ≥99%) were purchased from Sigma-Aldrich, Inc. (USA). Deionized water (DI water, 18 MΩ·cm) was used in the preparation of aqueous solutions (Ultra370, Younglin Co., Korea). All of the chemicals were commercially available and used without further purification.

Synthesis of Au NCs Orange fluorescent Au NCs were synthesized using glutathione (GS) as a thiolate ligand similarly to that previously reported.[1] Briefly, fresh aqueous solutions of 20 mM $HAuCl_4$ (2 mL) and 100 mM GS (0.6 mL) were added to 17.4 mL of DI water. Then, the aqueous mixture solution was vigorously stirred at room temperature for 1 minute. The mixture solution was then heated to 70 °C for 24 h, which forms strongly orange fluorescent Au NCs. Thereafter, the aqueous Au NCs solution was stored at 4 °C, and stable for at least 6 months without significant changes in their optical properties.

Preparation of Cd^{2+}-induced aggregates of Au(I)-GS complexes The aggregation of Au(I)-GS complexes has been induced by multivalent cations (*e.g.*, Cd^{2+}).[1,2] The Cd^{2+}-induced aggregation is ascribable to electrostatic and coordination interactions between the multivalent

Cd^{2+} cations and the monovalent carboxylic anions of GS in the Au(I)-GS complexes. Briefly, fresh aqueous solutions of 20 mM $HAuCl_4$ (2 mL) and 100 mM GS (0.8 mL) were mixed with 17.2 mL of DI water. The mixture solution was gently stirred at room temperature for 5 min. A white precipitate was formed in the mixture solution. The pH of the mixture solution was adjusted to pH 7 using a fresh 0.5 M NaOH. Then, the white precipitate disappeared and the solution became clear. The mixture was aged at room temperature for 1 h, and then stored at 4 ^{o}C. The formed Au(I)-GS complexes were stable for at least 3 months with negligible changes. For the Cd^{2+}-induced aggregation of the Au(I)-GS complexes, 25 μL of 1.6 M $Cd(NO_3)_2$ solution was added to 5 mL of the Au(I)-GS complex solution. The mixture solution was aged at 4 ^{o}C for 24 h, and then centrifugated to remove any precipitate formed in the solution.

Reduction of as-synthesized Au NCs with $NaBH_4$ as reducing agent The as-synthesized Au NCs were reduced using $NaBH_4$ as reducing agent. 300 μL of 0.8 M $NaBH_4$ solution was added to 15 mL of the as-synthesized Au NCs. The mixture solution was reacted at room temperature for 3 h under vigorous stirring in a closed vial, which resulted in color change of the solution from yellow to brown. This color change indicates further reduction of the as-synthesized Au NCs. The reduced Au NCs solution was aged at room temperature for 6 days, and stored at 4 ^{o}C.

Characterization Transmission electron microscope (TEM) images were collected using a Tecnai G2 F30 instrument (FEI Co., USA) operating at 300 kV. TEM samples were prepared by dropping aqueous sample solutions onto 400 mesh carbon-coated copper grids (Ted Pella Inc., USA) followed by drying in air. UV-Vis absorption and photoluminescence (PL) spectra were obtained using an Agilent 8453 UV-vis spectrometer (Agilent Tech., USA) and a FS-2 fluorescence spectrometer (Scinco Co., South Korea), respectively. For time-resolved PL spectra, aqueous sample solutions were excited by the second harmonic (355 nm) of a cavity-dumped oscillator (Mira/PulseSwitch, Coherent, 1 MHz, 710 nm, 150 fs). Emission was collected by using a set of lenses, spectrally resolved using a monochromator, detected using a photomultiplier, and recorded with a time-correlated single-photon counter (TCSPC, PicoHarp, PicoQuant). The instrumental response of the entire system was 0.05 ns. X-ray photoelectron spectroscopy (XPS) measurements were performed with a K-Alpha X-ray photoelectron spectrometer (Thermo Electron, USA) using Al Kα radiation ($h\nu$ = 1486.6 eV). XPS samples were prepared by dropping aqueous sample solutions on Si wafers and allowing them to dry. All electrochemical measurements were carried out using a CHI440A potentiostat (CH Instruments, Inc., USA) with a three-electrode cell. A glassy carbon electrode (diameter: 3 mm) was used as the working electrode. A Ag/AgCl (3 M NaCl) electrode and a Pt wire were used as the reference and counter electrode, respectively. Especially, for ECL measurements, the three-electrode cell was connected to the slit of a monochromator (Acton Standard SP2150, Princeton Instruments, U.S.A.) equipped with a charge-coupled device camera (PIXIS 100B, Princeton Instruments, U.S.A.).

References

1. Z. Luo, X. Yuan, Y. Yu, Q. Zhang, D. T. Leong, J. Y. Lee and J. Xie, *J. Am. Chem. Soc.* 2012, **134**, 16662-16670.

2. O. Raize, Y. Argaman and S. Yannai, *Biotechnol. Bioeng.* 2004, **87**, 451-458.

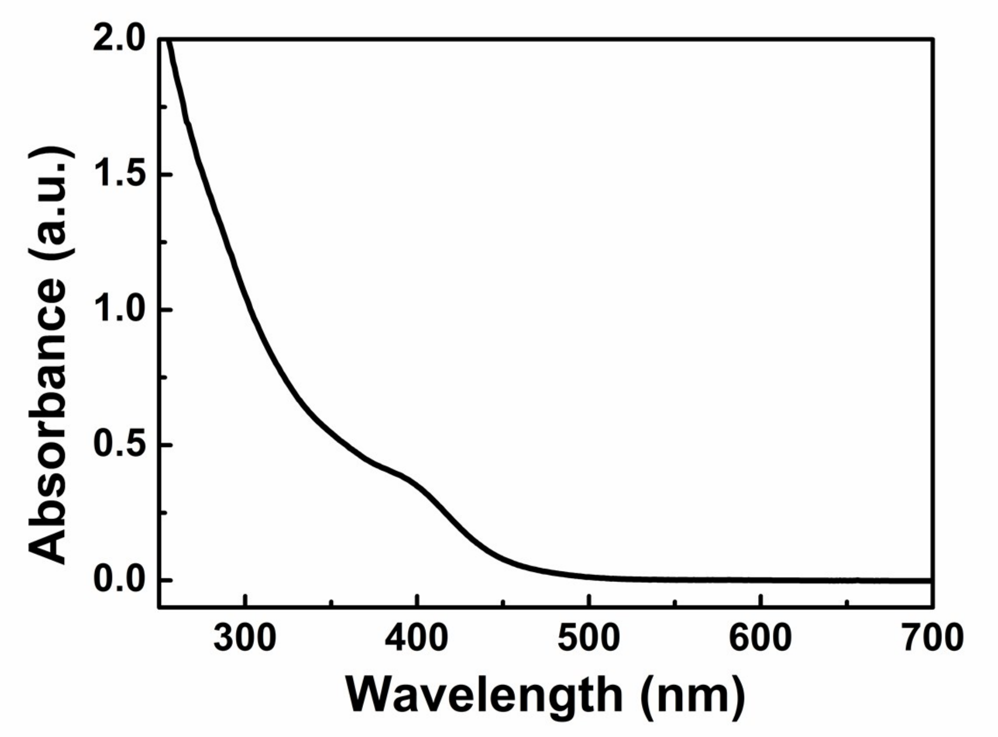

Figure S1. UV-Vis absorption spectrum of as-synthesized Au NCs.

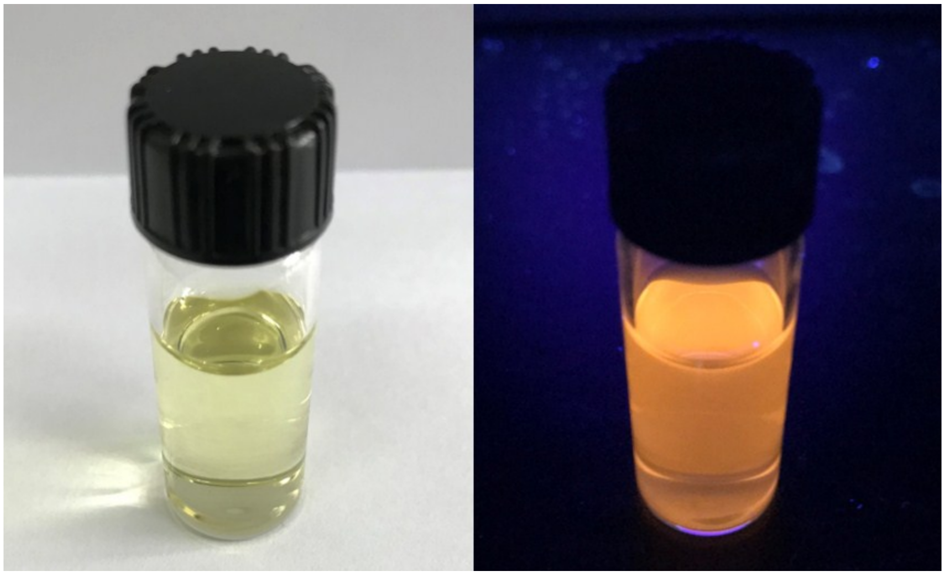

Figure S2. Optical images of as-synthesized Au NCs under (left) visible and (right) UV light.

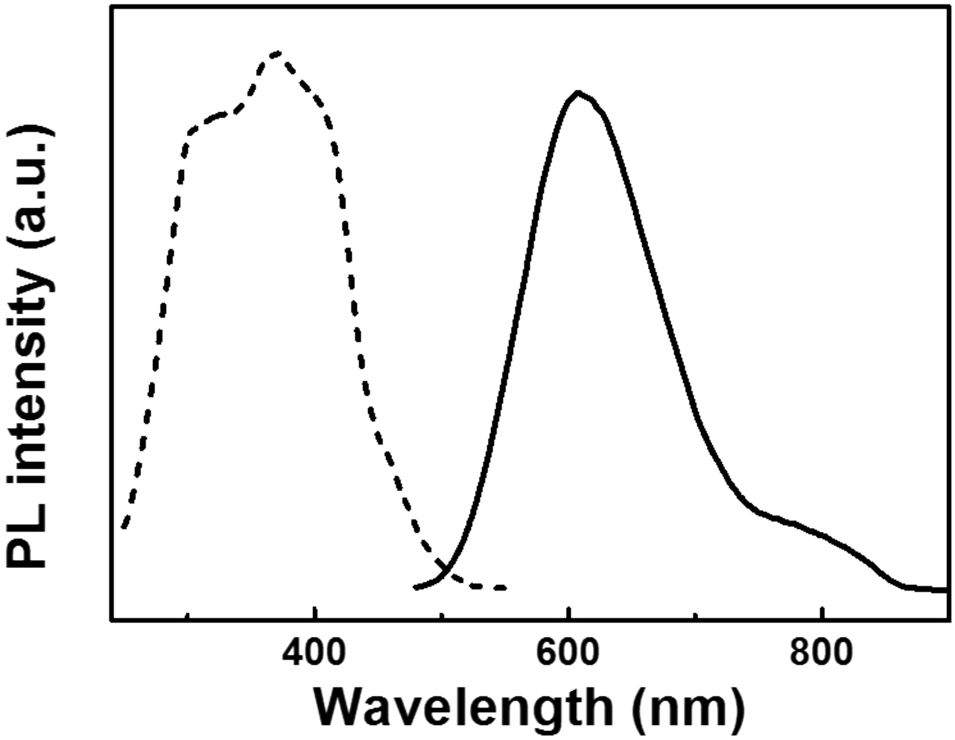

Figure S3. Photoexcitation (dotted line, λ_{em} = 610 nm) and photoemission (solid line, λ_{ex} = 365 nm) spectra of as-synthesized Au NCs. For comparison, the photoemission spectrum, shown in Figure 1B, of as-synthesized Au NCs is re-presented together with the photoexcitation spectrum of as-synthesized Au NCs.

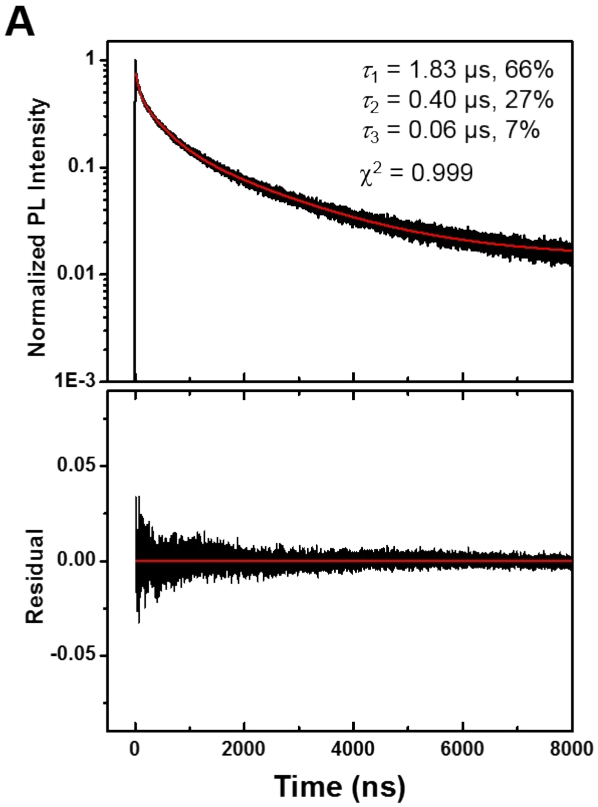

Figure S4. Time-resolved photoemission of as-synthesized Au NCs at (A) 610 nm and (B) 790 nm. The decay profiles were fitted by the multi-exponential models with microsecond-scale and nanosecond-scale lifetimes, respectively. The upper portion of each image is an exponential fit of the experimental decay profile, and the lower portion of each image shows the residual of fitting.

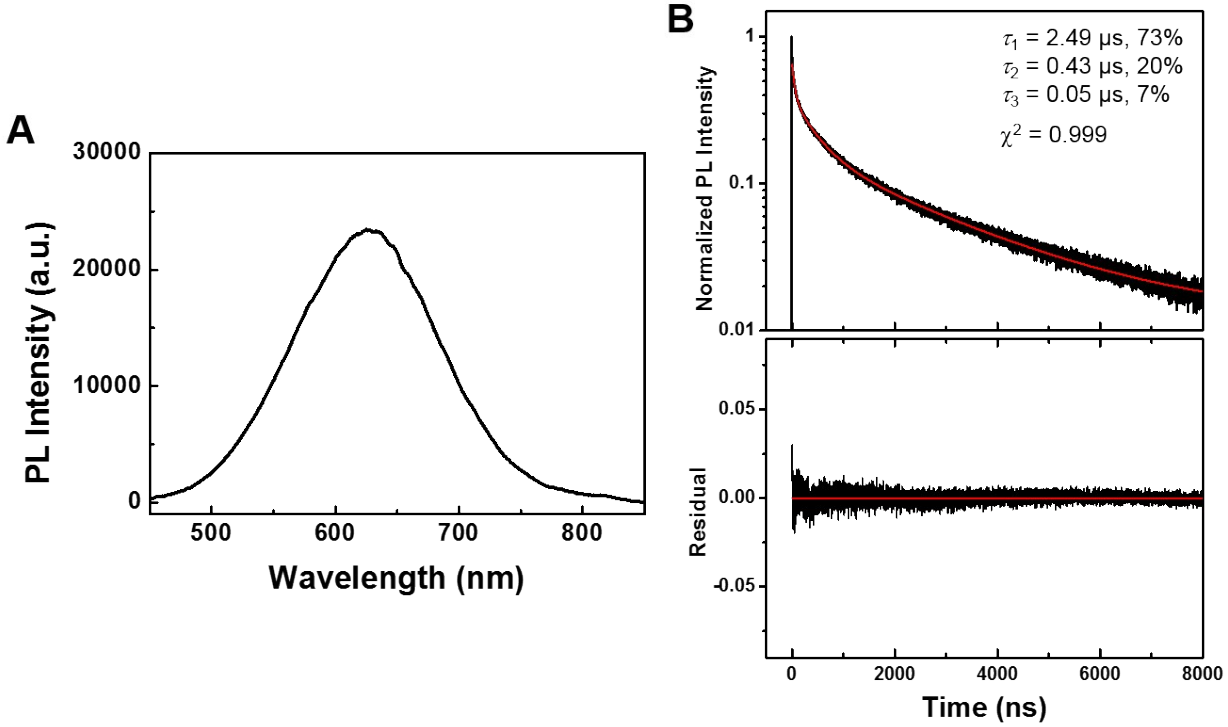

Figure S5. (A) Photoemission spectrum and (B) time-resolved photoemission of Cd^{2+}-induced aggregates of the Au(I)-GS complexes. The decay profile monitored at 610 nm was fitted by the multi-exponential models with microsecond-scale lifetimes. The upper portion of (B) is an exponential fit of the experimental decay profile, and the lower portion of (B) shows the residual of fitting.

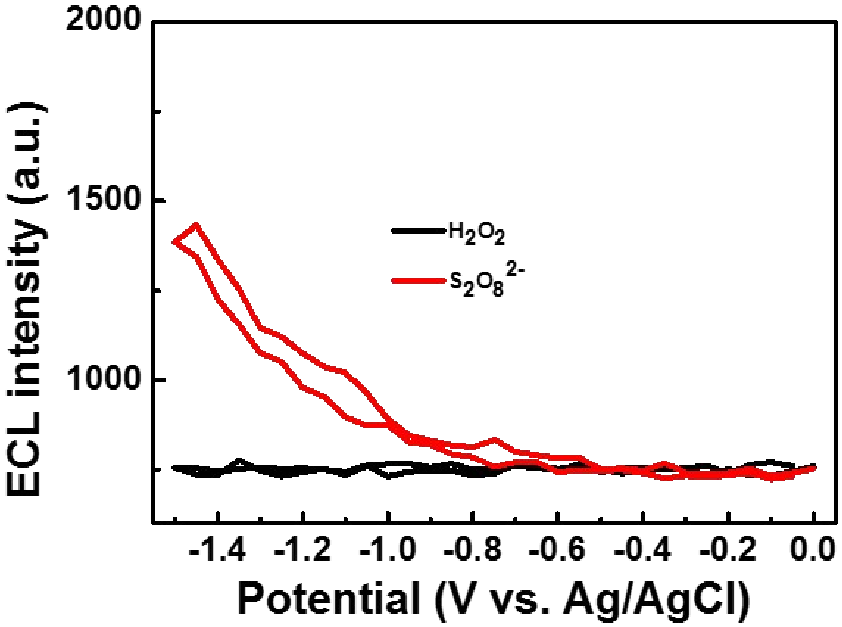

Figure S6. ECL-potential curves of as-synthesized Au NCs in water containing 0.1 M KNO_3 in the presence of (black line) 0.5 M H_2O_2 or (red line) 0.1 M $S_2O_8^{2-}$ as cathodic co-reactant. Scan rate: 25 mV/s.

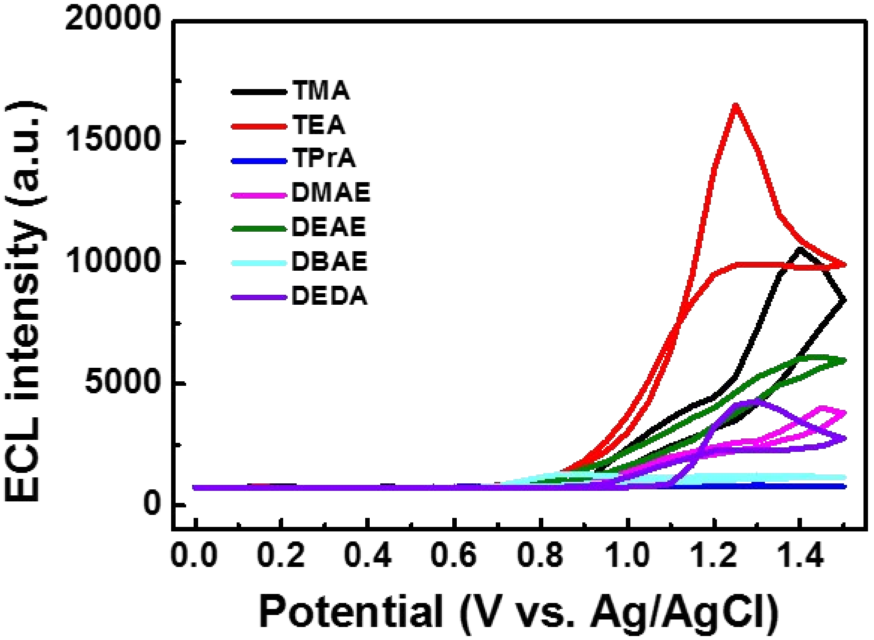

Figure S7. ECL-potential curves of as-synthesized Au NCs in water containing 0.1 M KNO_3 in the presence of seven different anodic co-reactants (specifically, trimethylamine (TMA), triethylamine (TEA), tripropylamine (TPA), 2-(dimethylamino)ethanol (DMAE), 2-(diethylamino)ethanol (DEAE), 2-(dibutylamino)ethanol (DBAE), and *N*,*N*-diethylethylenediamine (DEDA)). Co-reactant concentration: 0.5 M. For comparison, the ECL-potential curve, shown in Figure 2A, of as-synthesized Au NCs obtained in the presence of TEA co-reactant is re-presented (red solid line) together with other curves obtained with other co-reactants. Scan rate: 25 mV/s.

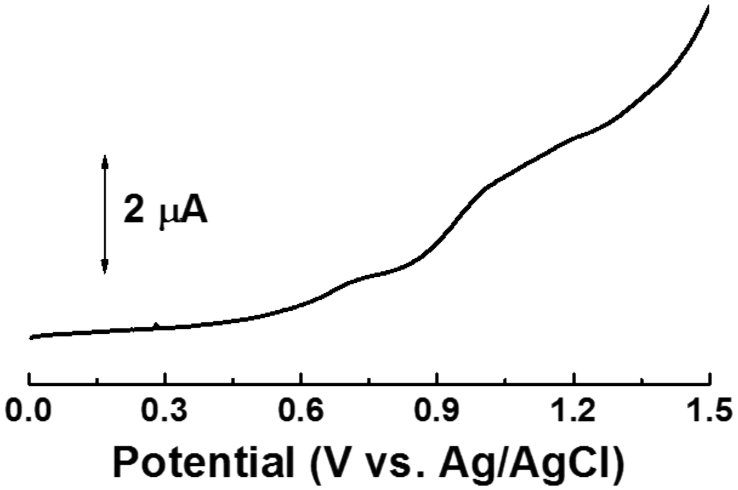

Figure S8. Differential pulse voltammogram (DPV) of as-synthesized Au NCs in water containing 0.1 M KNO_3. Pulse amplitude: 50 mV. Scan rate: 10 mV/s. In the anodic region, two peaks at *ca.* 0.8 and *ca.* 1.0 V were observed, corresponding to electrochemical oxidation of Au(0)-GS and Au(I)-GS motifs, respectively, in the as-synthesized Au NCs.

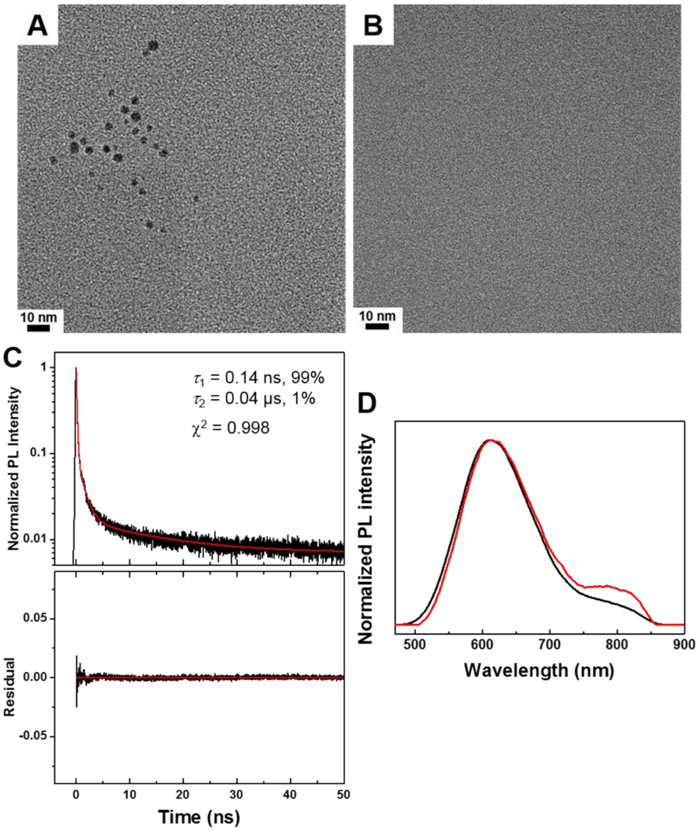

Figure S9. TEM images of (A) reduced Au NCs and (B) Cd^{2+}-induced aggregates of the Au(I)-GS complexes. Since we did not have access to TEM with sufficient resolution and contrast to image unreduced metal ionic species such as Cd^{2+}-induced aggregates of the Au(I)-GS complexes, no distinct NC particles are observed in (B). But we observed the increase in the size of NCs in (A) due to the increase in the Au(0) contents of the reduced Au NCs compared to that of the as-synthesized Au NCs. (C) Time-resolved photoemission profile of reduced Au NCs at 790 nm. The decay profile monitored at 790 nm was fitted by the multi-exponential model with nanosecond-scale lifetimes. The upper portion is an exponential fit of the experimental decay profile, and the lower portion shows the residual of fitting. (D) Normalized photoemission spectra of reduced Au NCs (red line) and as-synthesized Au NCs (black line). For comparison, the normalized photoemission spectrum, shown in Figure 1B, of as-synthesized Au NCs is represented together with that of reduced Au NCs.