Electronic Supplementary Information

Hydroxyl Radical-Induced Etching of Glutathione-Capped Gold Nanoparticles to Oligomeric Au^{I}-Thiolate Complexes

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Calculation

The fermi energy (E_{Fermi}) of gold is approximately 5.5 eV. The gold nanolcusters preferentially contain a magnic number (N) of atoms, including 2, 5, 8, 11, 13, 18, 22, 25, 28, 39, 55, and so on. According to the sphericla Jellium model, $E_{Fermi}/N^{1/3}$,

the emission maxima of Au_2 is

$$5.5 \text{ eV}/2^{1/3} = 4.37 \text{ eV} = 284 \text{ nm},$$

the emission maxim of Au_5 is

$$5.5 \text{ eV}/5^{1/3} = 3.22 \text{ eV} = 385 \text{ nm},$$

the emission maxima of Au_8 is

$$5.5 \text{ eV}/8^{1/3} = 2.75 \text{ eV} = 450 \text{ nm},$$

the emission maxima of Au_{11} is

$$5.5 \text{ eV}/11^{1/3} = 2.47 \text{ eV} = 502 \text{ nm},$$

and, the emission maxima of Au_{13} is

$$5.5 \text{ eV}/25^{1/3} = 2.34 \text{ eV} = 530 \text{ nm}.$$

Because trypsin-, lysozyme-, and glucose oxidase-stabilized gold nanoclusters exhibited emission maxima at 415, 460, and 535 nm, we assert that trypsin-, lysozyme-, and glucose oxidase-stabilized gold nanoclusters correspond to Au_5, Au_8, and Au_{13} clusters, respectively.

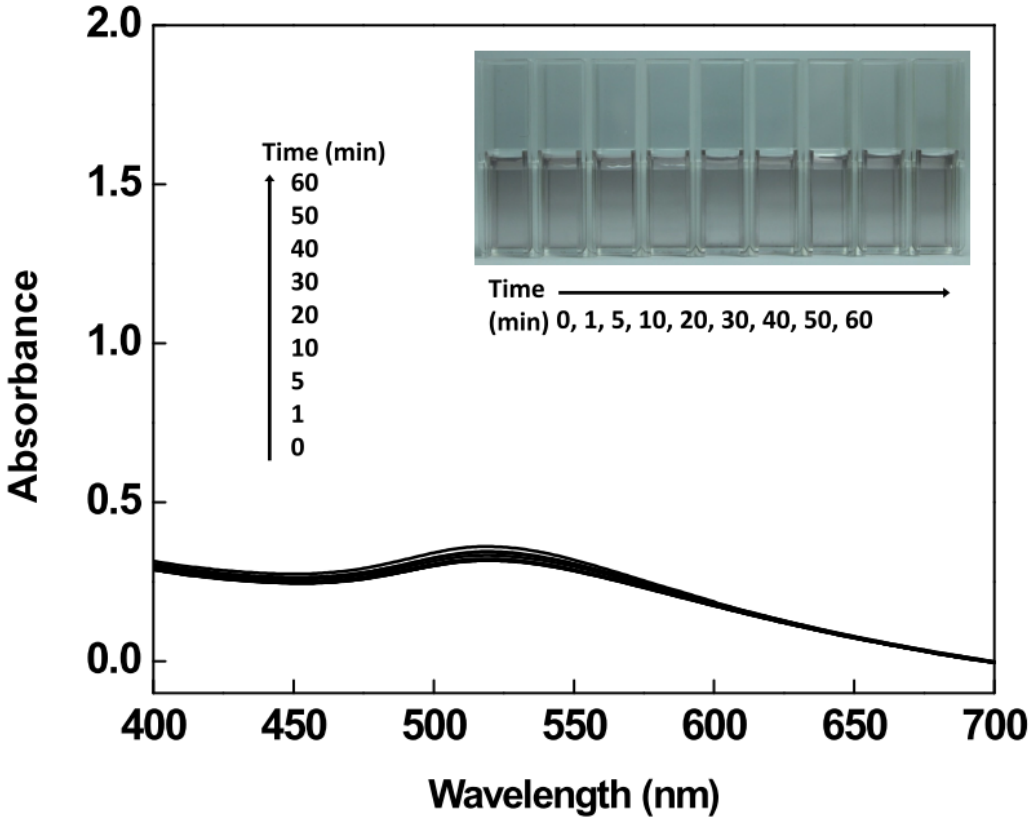

Figure S1. Time evolution of visible spectra of a mixture of GSH-AuNPs and 5 mM Fe^{II}.

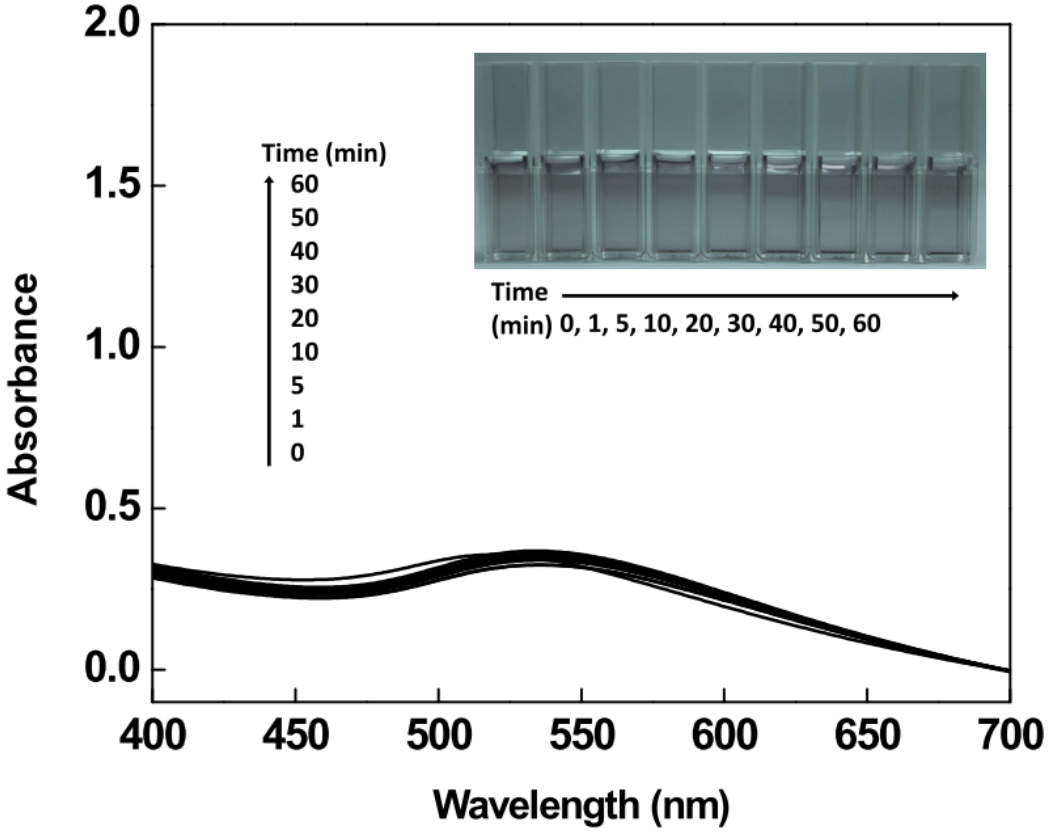

Figure S2. Time evolution of visible spectra of a mixture of GSH-AuNPs and 100 mM H_2O_2.

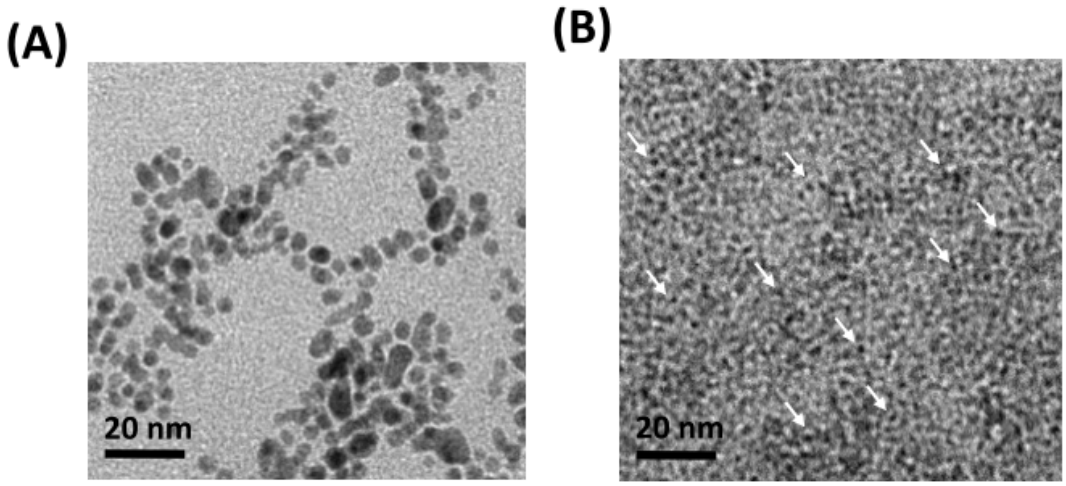

Figure S3. TEM imges of GSH-AuNPs (A) before and (B) after treatement of Fenton reagent for 1 h.

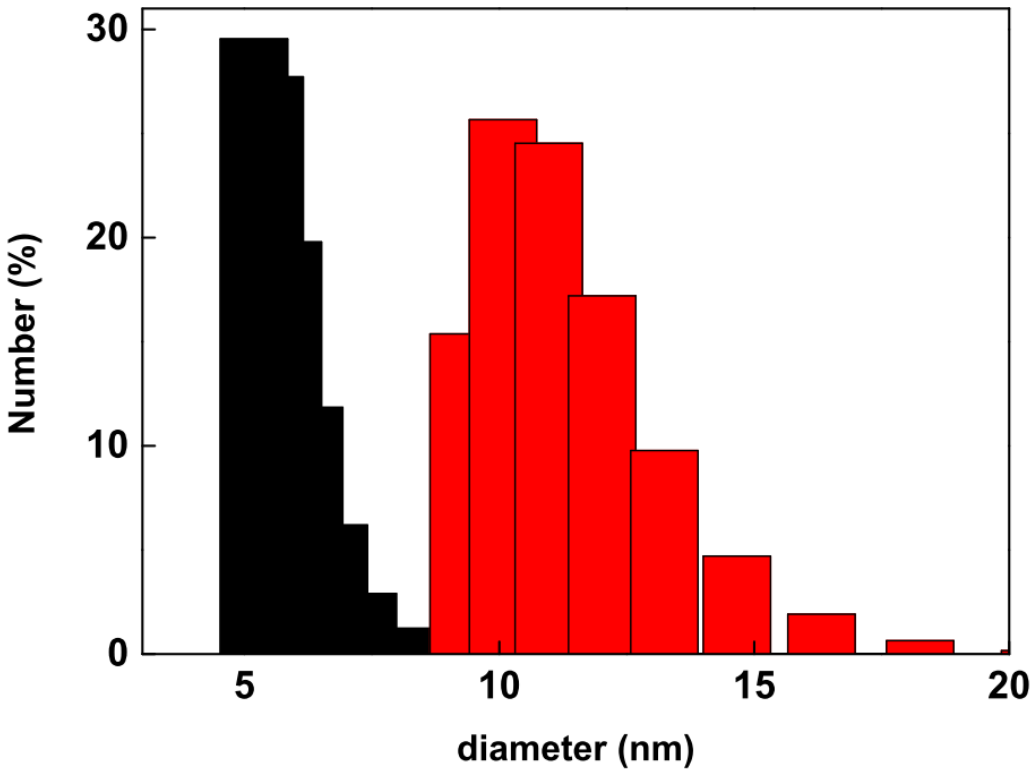

Figure S4. DLS spectra of GSH-AuNS before (red color) and after (black color) the addition of Fenton's solution. Fenton's reagent contains 5 mM Fe^{II} and 100 mM H_2O_2.

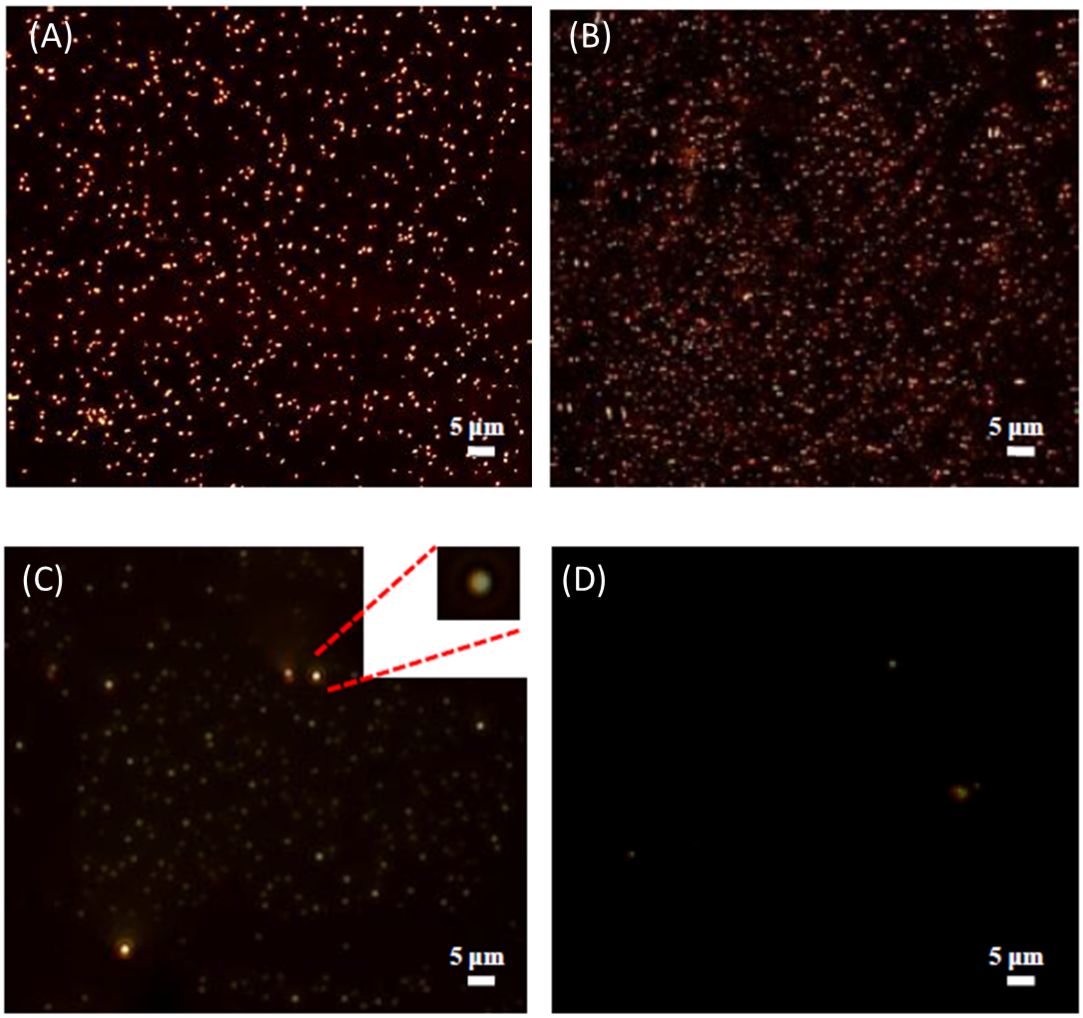

Figure S5. Scattering images of the products obtained from the incubation of 100 nm-sized gold nanospheres and Fenton's solution at (A) 10 s, (B) 30 min, (C) 1 h, and (D) 3 h. Exposure times, 50 ms; scattering detection area using a 40× objective, 860 µm × 610 µm corresponding to 4080 (horizontal) × 3072 (vertical) pixels.

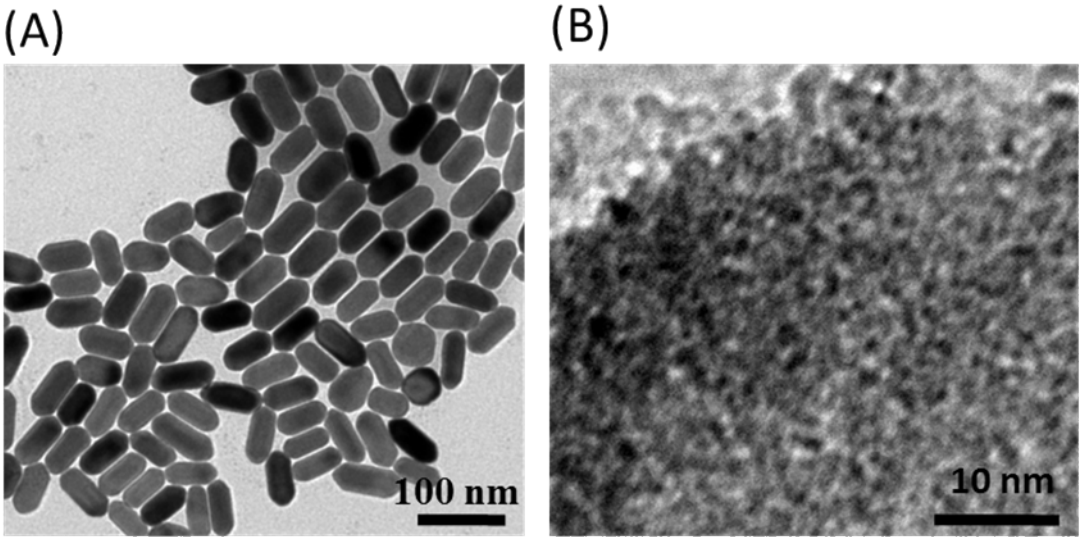

Figure S6. (A, B) TEM images of short gold nanorods (A) before and (B) after the addition of Fenton's solution.

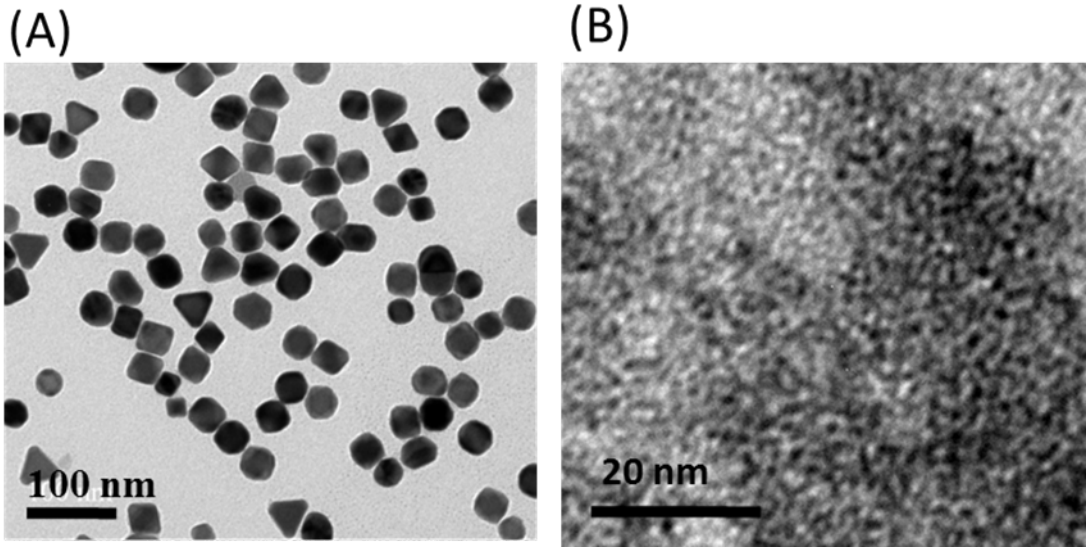

Figure S7. (A, B) TEM images of octahedral gold nanocrystals (A) before and (B) after the addition of Fenton's solution.

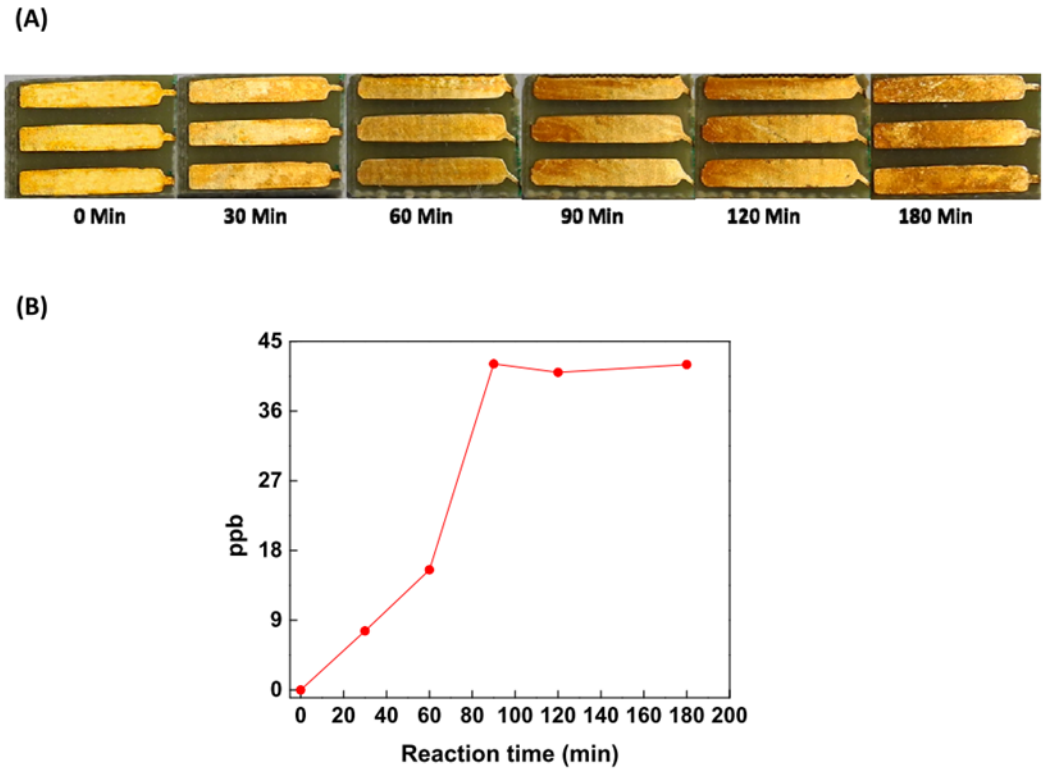

Figure S8. (A) Time evolution of photo images of electronic scraps in the presence of 5 mM Fe^{II} and 100 mM H_2O_2. (B) The concentrations of the liberated gold ions from electronic scraps as a function of time.

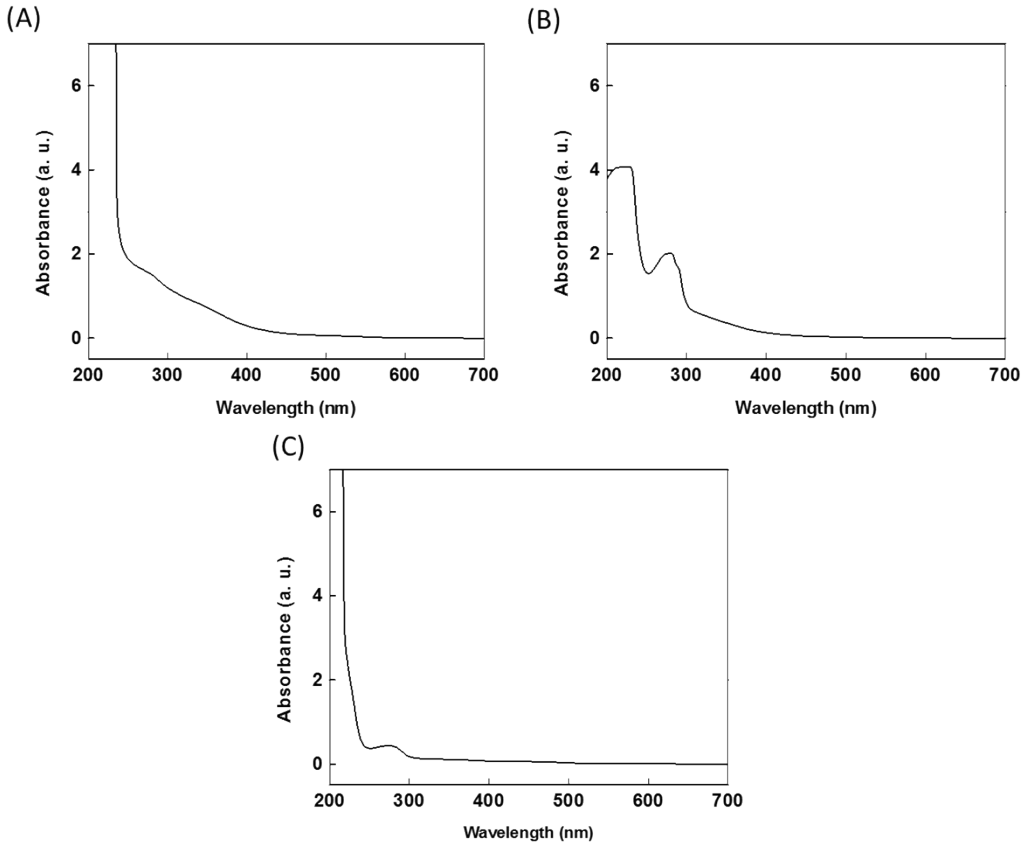

Figure S9. Absorption spectra obtained from incubation of (A) trypsin, (B) lysozyme, and (C) glucose oxidase with the oligomeric Au^{I}-thiolate complexes. Protein (25 mg/mL) reacted with the oligomeric Au^{I}-thiolate complexes at ambient temperature for 8 h.

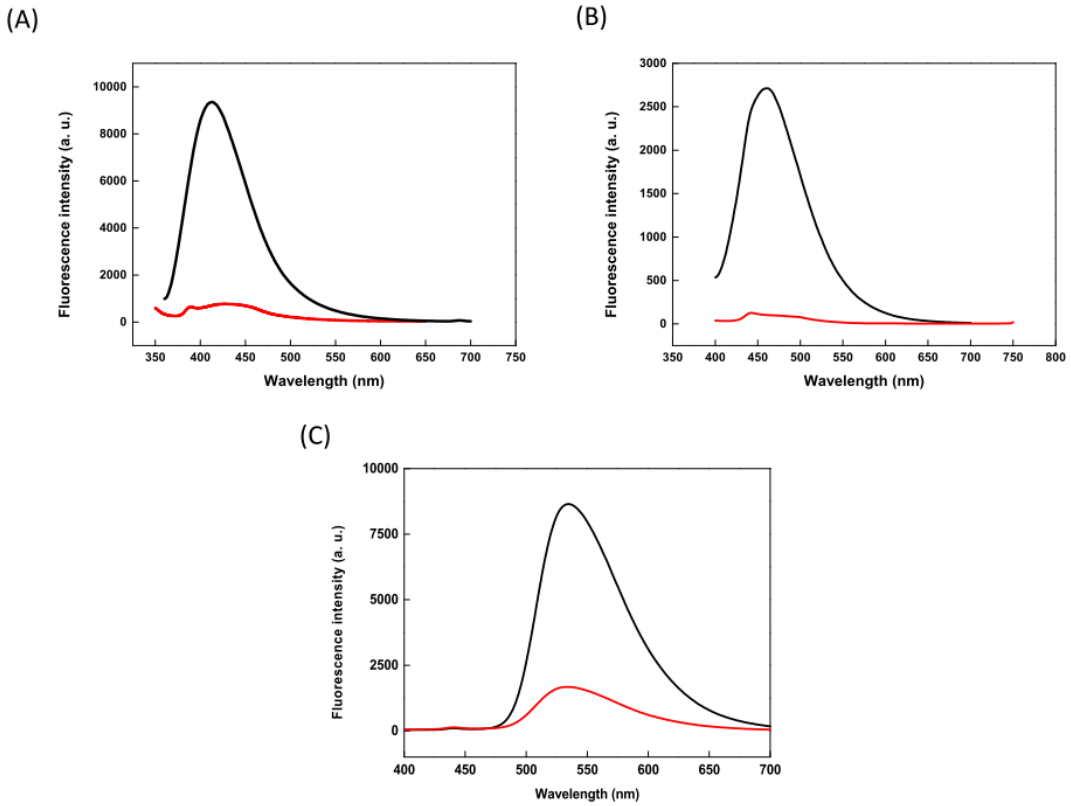

Figure S10. Fluorescence spectra of protein (red line) and protein-stabilized AuNCs (black line): (A) trypsin, (B) lysozyme, and (C) glucose oxidase.

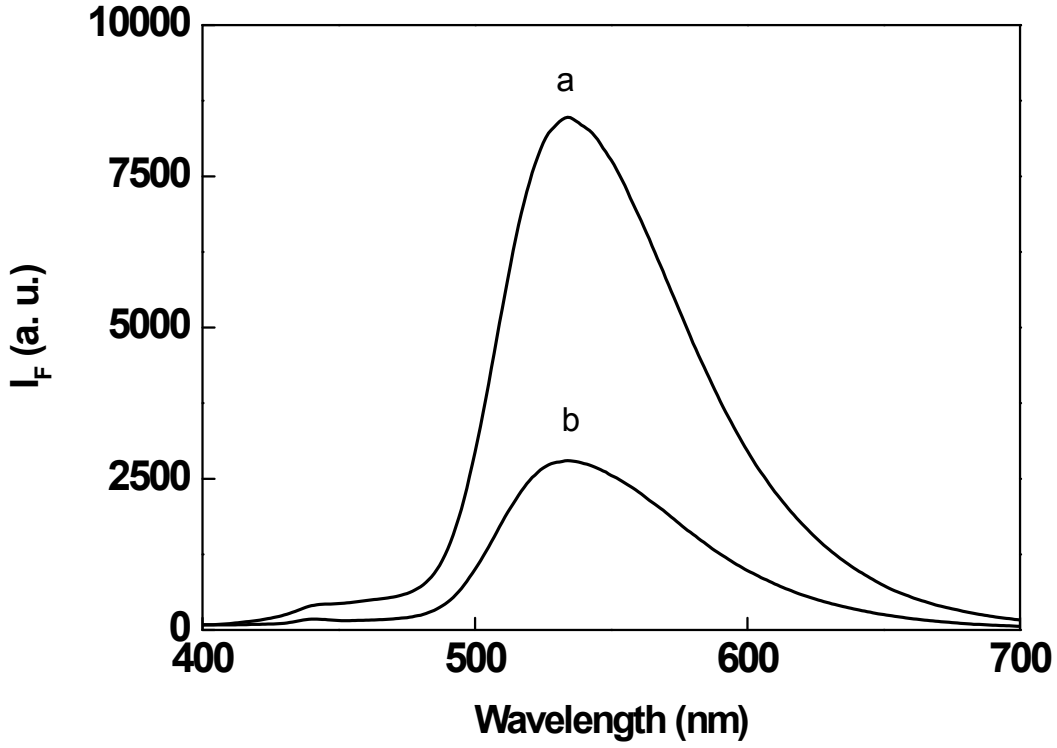

Figure S11. Fluorescence spectra of glucose oxidase-stabilized AuNCs (a) before and (b) after the addition of 100 μM Hg^{2+}.

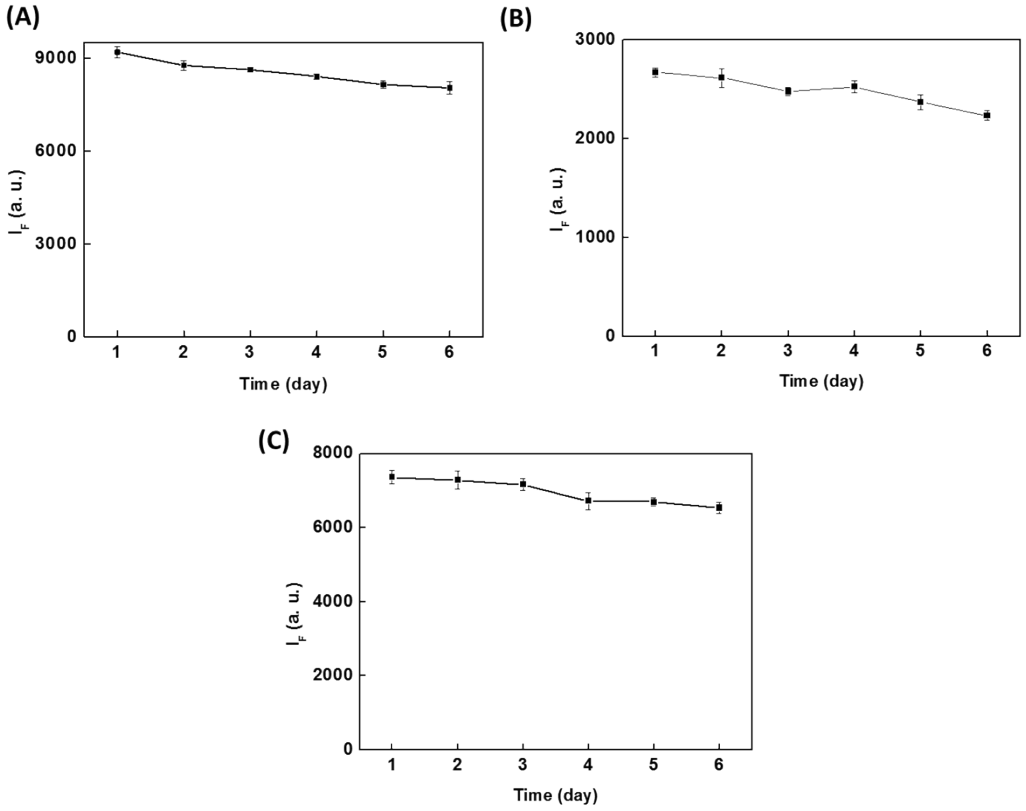

Figure S12. Effect of time on the fluorescence intensity at (A) 415, (B) 460, and (C) 535 nm of (A) trypsin-, (B) lysozyme-, and (C) glucose oxidase-stabilized AuNCs.

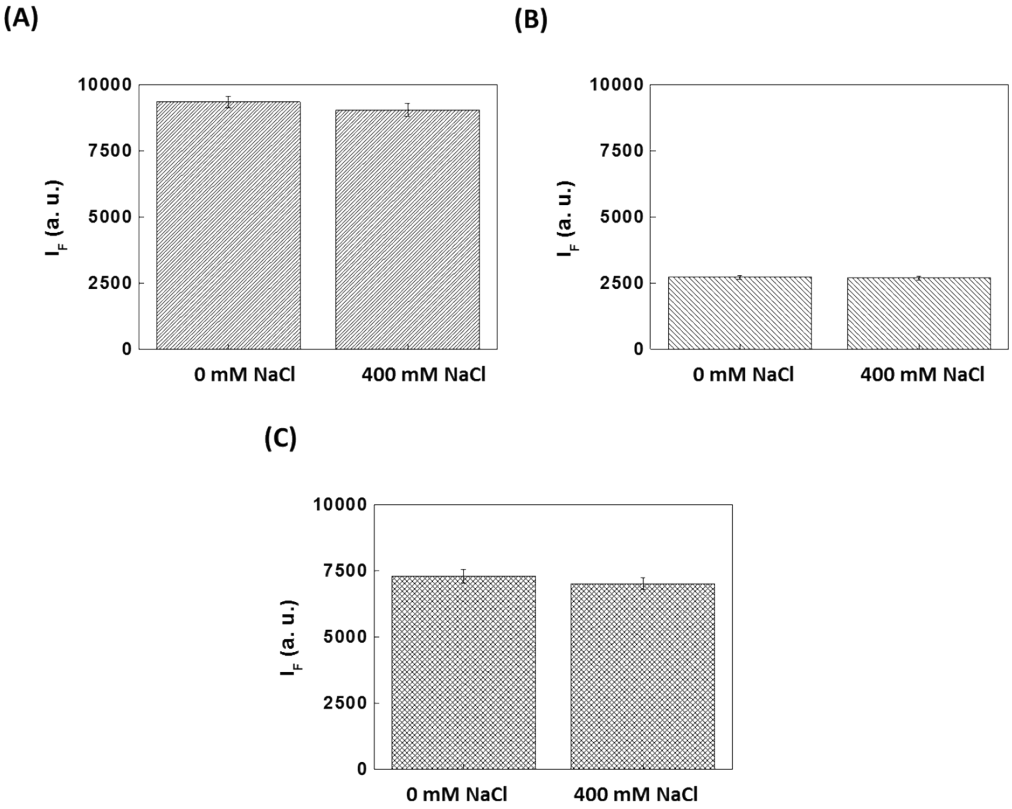

Figure S13. The fluorescence intensity at (A) 415, (B) 460, and (C) 535 nm of (A) trypsin-, (B) lysozyme-, and (C) glucose oxidase-stabilized AuNCs in the absence and presence of 400 mM NaCl.

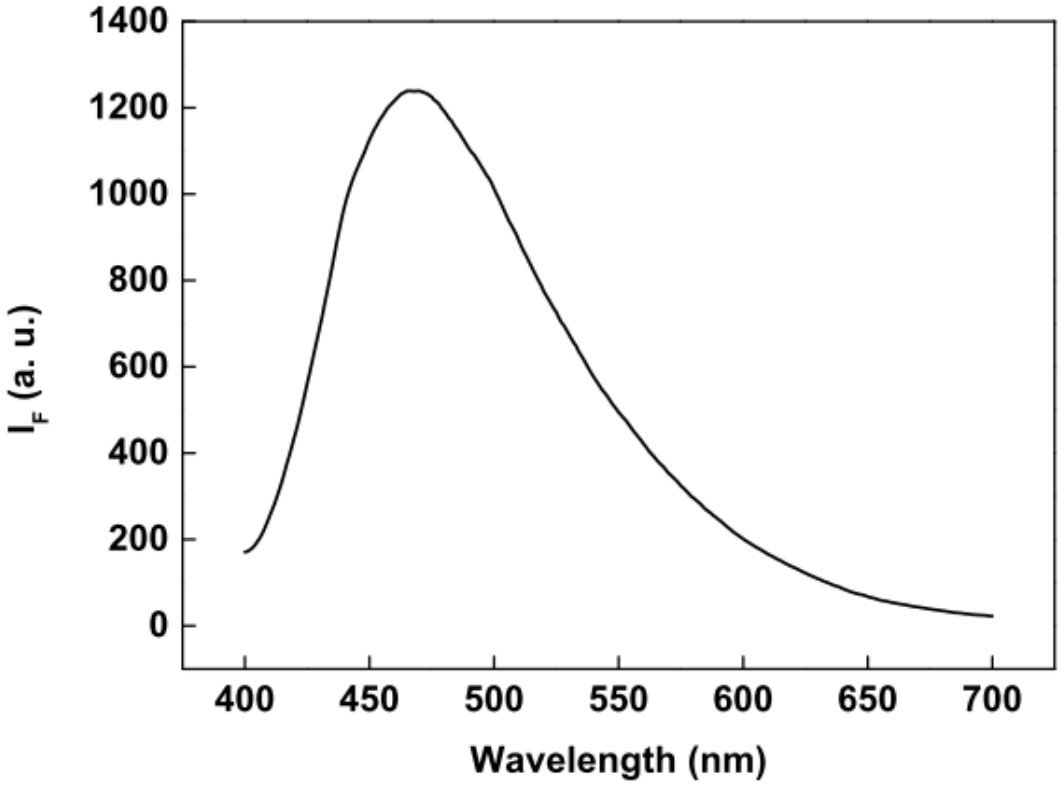

Figure S14. Fluorescence spectrum of bovine serum albumin-stabilized AuNCs. The excitation wavelength is 350 nm.

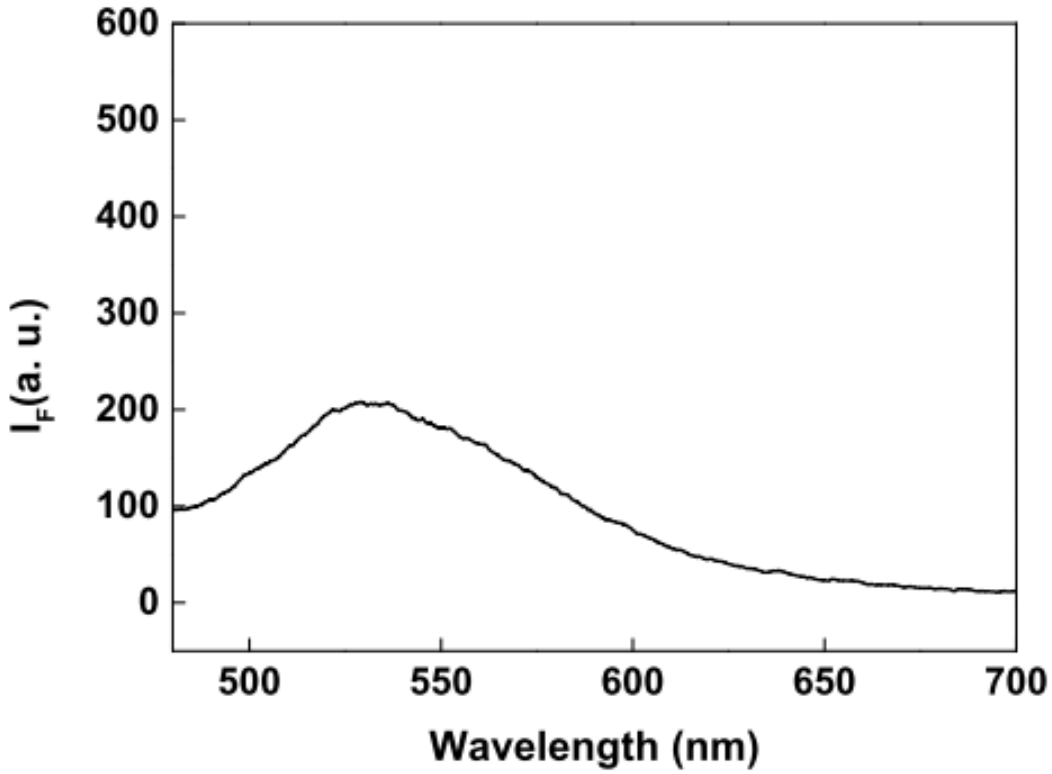

Figure S15. Fluorescence spectrum of choline oxidase-stabilized AuNCs. The excitation wavelength is 380 nm.

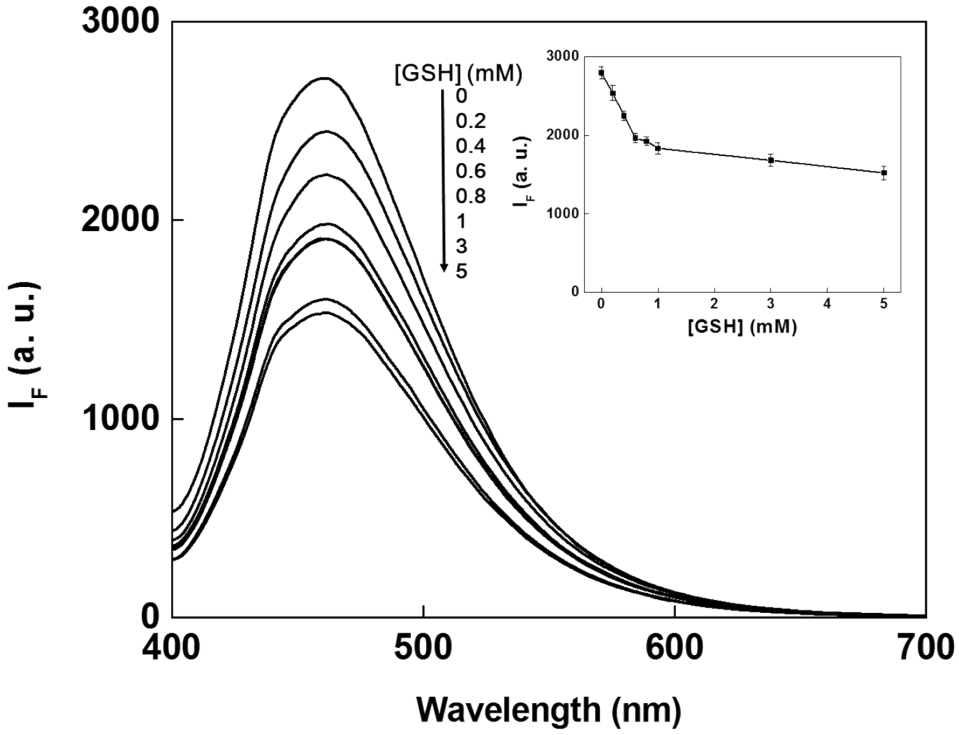

Figure S16. Fluorescence intensity at 460 nm of lysozyme-stabilized AuNCs in the presence of different concentrations of GSH. The incubation time is 15 min. Inset: a plot of the fluorescence intensity at 460 nm *versus* the GSH concentration.

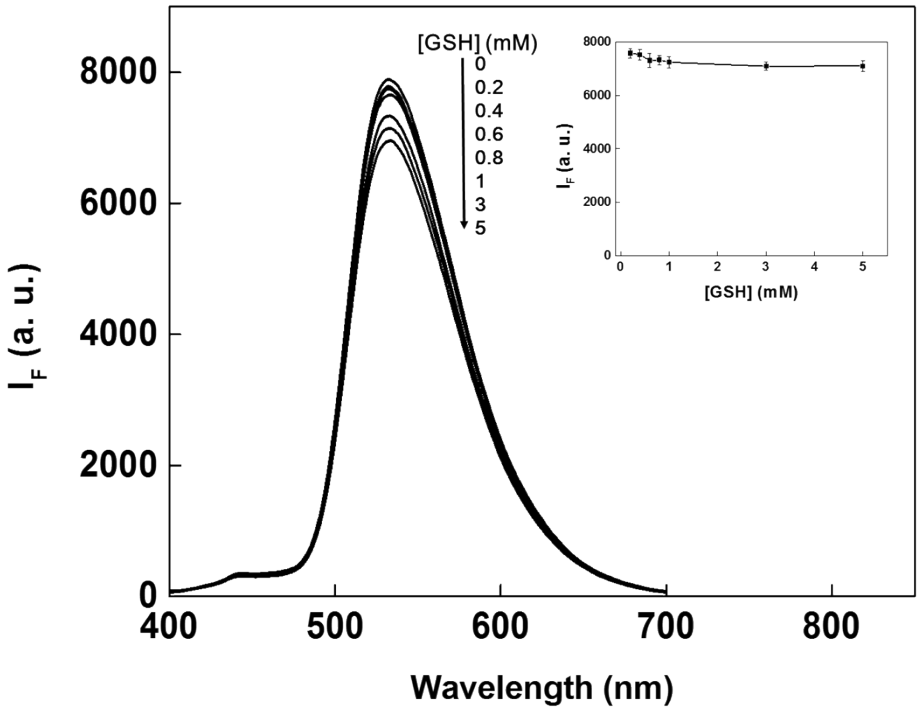

Figure S17. Fluorescence intensity at 535 nm of glucose oxidase-stabilized AuNCs in the presence of different concentrations of GSH. The incubation time is 15 min. Inset: a plot of the fluorescence intensity at 535 nm versus the GSH concentration.

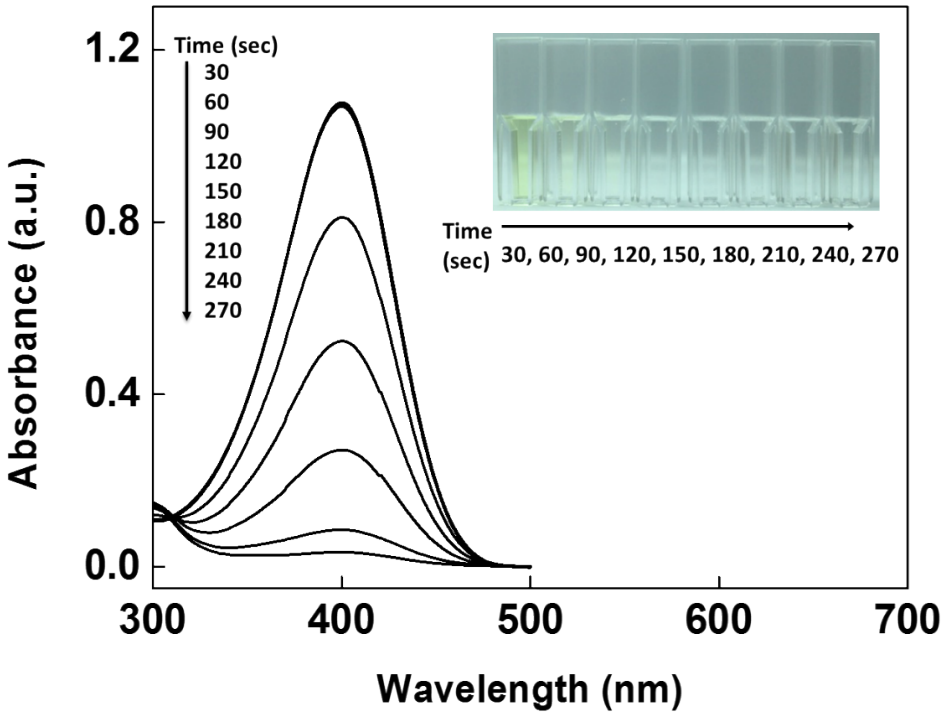

Figure S18. Time evolution of visible spectra of a mixture of 70 μM 4-nitrophenol and the oligomeric Au^{I}-thiolate complexes. This reaction proceeded at ambient temperature.