Supplementary Information

Ligand-ligand interactions effect on the formation of photoluminescent gold nanoclusters embedded in Au(I)-thiolate supramolecules

Hsiang-Yu Chang,[a] Yu-Ting Tseng,[a] Zhiqin Yuan,[b] Hung-Lung Chou,[*c] Ching-Hsiang Chen,[d] Bing-Joe Hwang,[d] Meng-Che Tsai,[d] Huan-Tsung Chang[*aeh] and Chih-Ching Huang[*fgh]

[a] *Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan*

[b] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

[c] *Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10617, Taiwan*

[d] *Nanoelectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10617, Taiwan*

[e] *Department of Chemistry, Chung Yuan Christian University, Taoyuan City 32023, Taiwan*

[f] *Department of Bioscience and Biotechnology, National Taiwan Ocean University, Keelung 20224, Taiwan*

[g] *Center of Excellence for the Oceans, National Taiwan Ocean University, Keelung 20224, Taiwan*

[h] *School of Pharmacy, College of Pharmacy, Kaohsiung Medical University, Kaohsiung 80708, Taiwan*

Correspondence: Professor Hung-Lung Chou, Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, Taipei 10617, Taiwan. E-mail: HLCHOU@mail.ntust.edu.tw; Professor Huan-Tsung Chang, Department of Chemistry, National Taiwan University, 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan. E-mail: changht@ntu.edu.tw; Professor Chih-Ching Huang, Department of Bioscience and Biotechnology, National Taiwan Ocean University, 2, Beining Road, Keelung 20224, Taiwan. E-mail: huanging@ntou.edu.tw

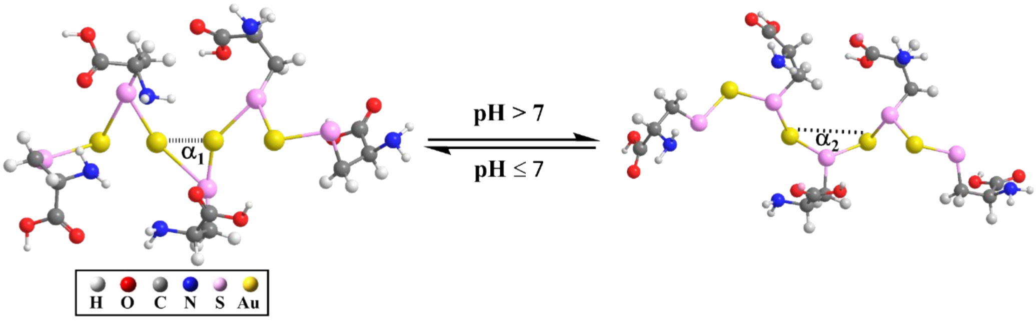
Table S1 The intensities of static light scattering and zeta potentials of the products from the reactions of $HAuCl_4$ (1.4 mM) with L-cysteine (10 mM) at pH of (A) 3, (B) 5, (C) 7, and (D) 9.

Sample	Static light scattering (kcps; n = 5)	Zeta potential (mV; n =5)
A	273.2±32.7	−0.92±4.75
B	243.2±25.6	−1.14±4.04
C	250.2±22.3	−4.53±3.70
D	74.2±18.3	−12.3±2.23

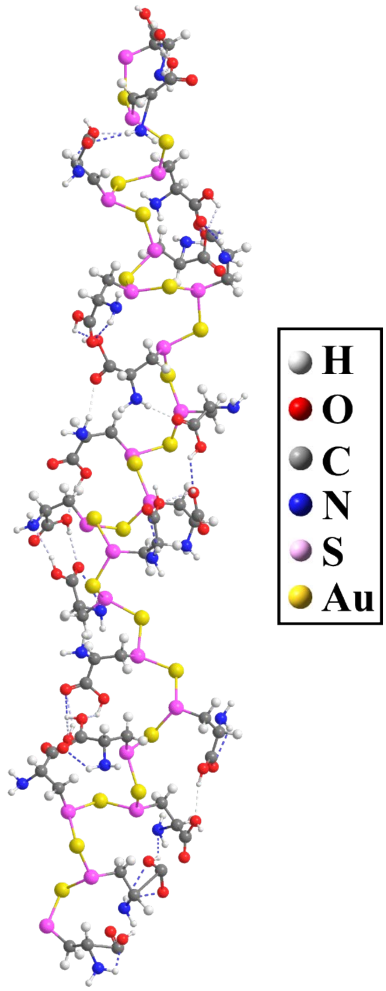
Table S2 Optical properties of as-prepared Cys–Au NCs_{pH3-7} and $-[Cys-Au(I)]_n-_{pH9}$.

sample	λ_{max}^{abs} (nm)[a]	λ_{max}^{ex} (nm)[b]	λ_{max}^{em} (nm)[c]	QY (%)	τ (τ_1/τ_2, ns)
Cys–Au NCs_{pH3}	365	355	630	11.6	218.68 (29.05%)/2288.78 (70.95%)
Cys–Au NCs_{pH5}	365	350	630	10.4	44.27 (39.72%)/1876.49 (60.28%)
Cys–Au NCs_{pH7}	365	350	630	10.1	145.07 (32.59%)/2190.04 (67.41%)
$-[Cys-Au(I)]_n-_{pH9}$	-	-	-	0.21	42.97 (63.51%)/1196.65 (36.49%)

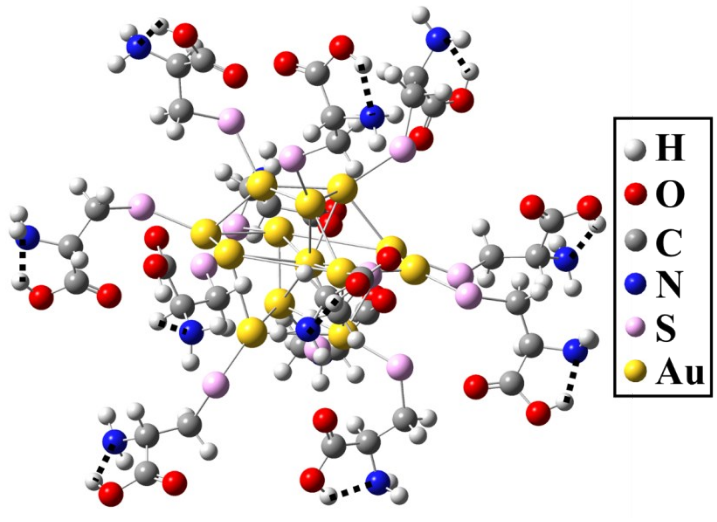
[a]absorption-band maxima at wavelength. [b]excitation-band maxima at wavelength. [c]emission-band maxima at wavelength.



Scheme S1 Schematic of aurophilic Au(I)···Au(I) interactions mediated by the interaction between adjacent Cys ligands along the –[Cys–Au(I)]$_n$– polymeric backbone through controlling solution pH values. Parameters α_1 and α_2 are the Au(I)–S(R)–Au(I) angles at pH ≤ 7 and pH > 7, respectively.



Scheme S2 Schematic of a helical structure of the $-[\text{Cys}-\text{Au(I)}]_n-$ polymer.



Scheme S3 Proposed structure of $[Au_{13}Cys_{12}]^+$.

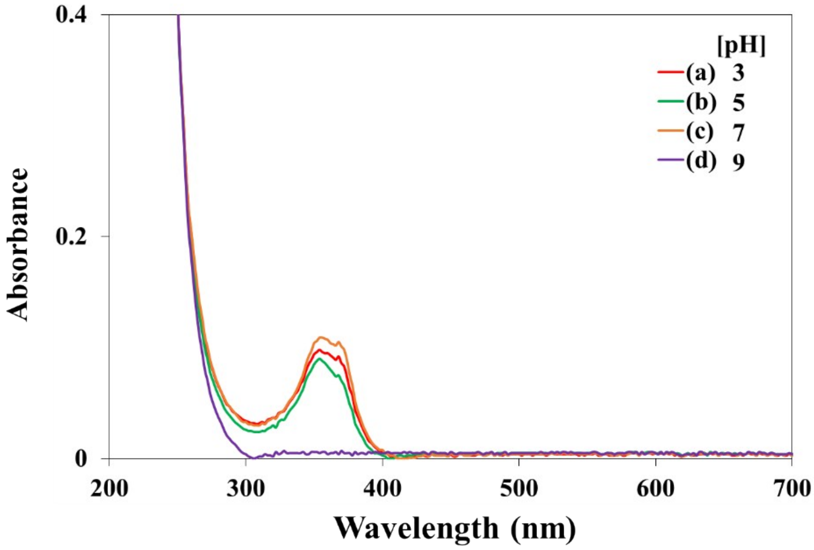


Fig. S1 UV–Vis absorption spectra of the products from the reactions of $HAuCl_4$ (1.4 mM) with L-cysteine (10 mM) for 1 h in solutions with pH at (a) 3, (b) 5, (c) 7, and (d) 9.

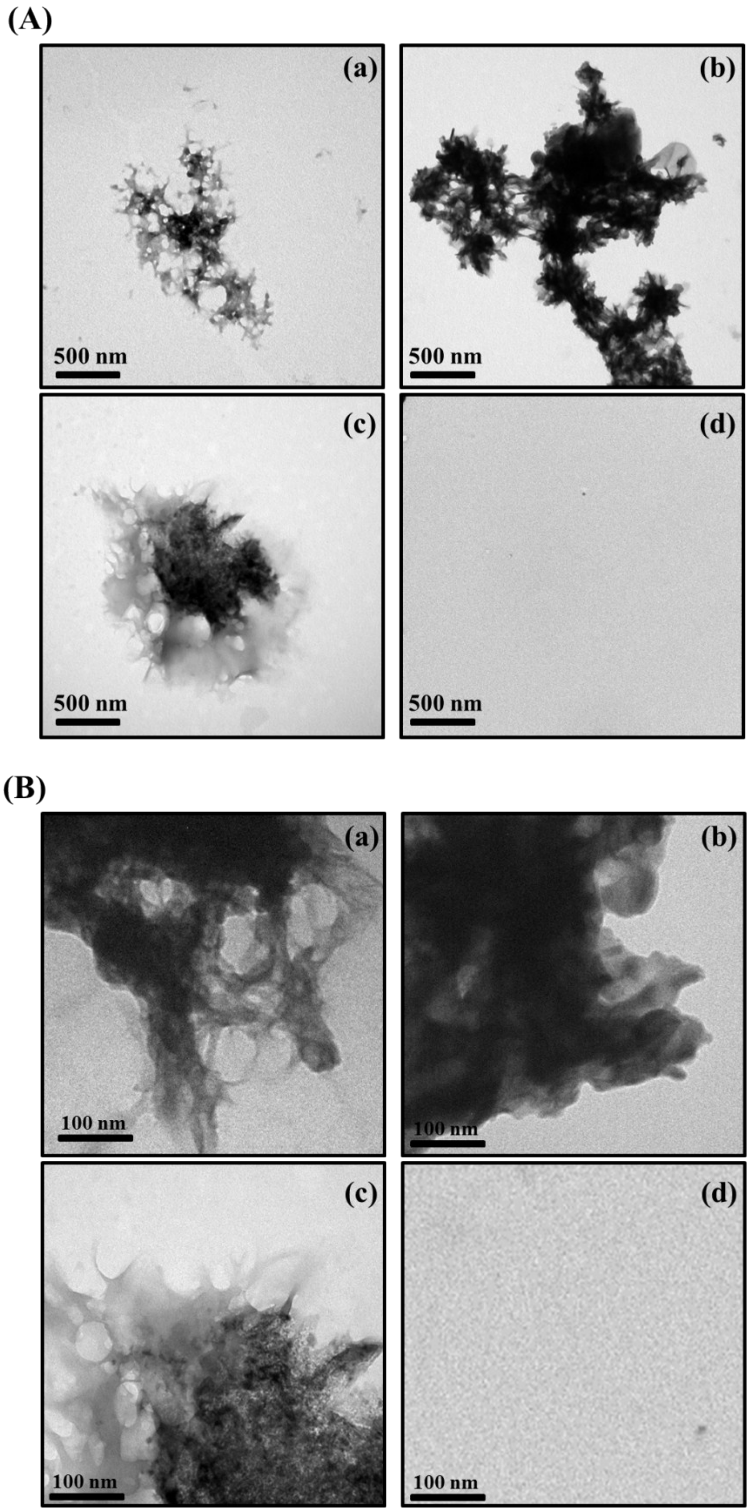


Fig. S2 (A) Low-magnification and (B) high-magnification TEM images of the products from the reactions of $HAuCl_4$ (1.4 mM) with L-cysteine (10 mM) for 1 h in solutions at pH (a) 3, (b) 5, (c) 7, and (d) 9.

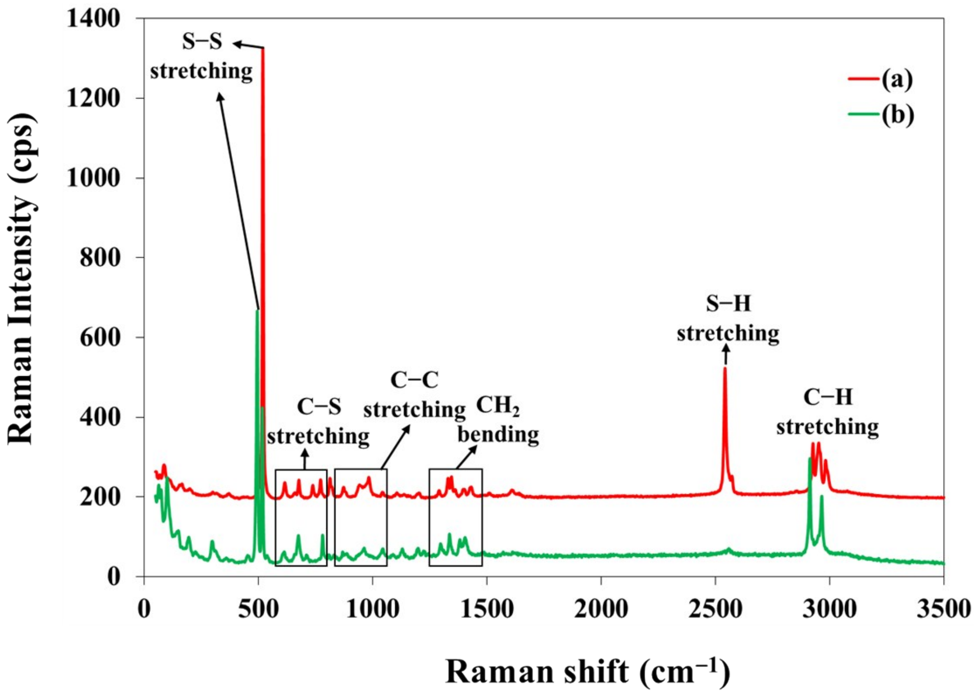


Fig. S3 Raman spectra of (a) L-Cys and (b) as-prepared −[Cys−Au(I)]$_n$− supramolecules from the reaction of $HAuCl_4$ (1.4 mM) with L-cysteine (10 mM) for 1 h in a solution at pH 3.

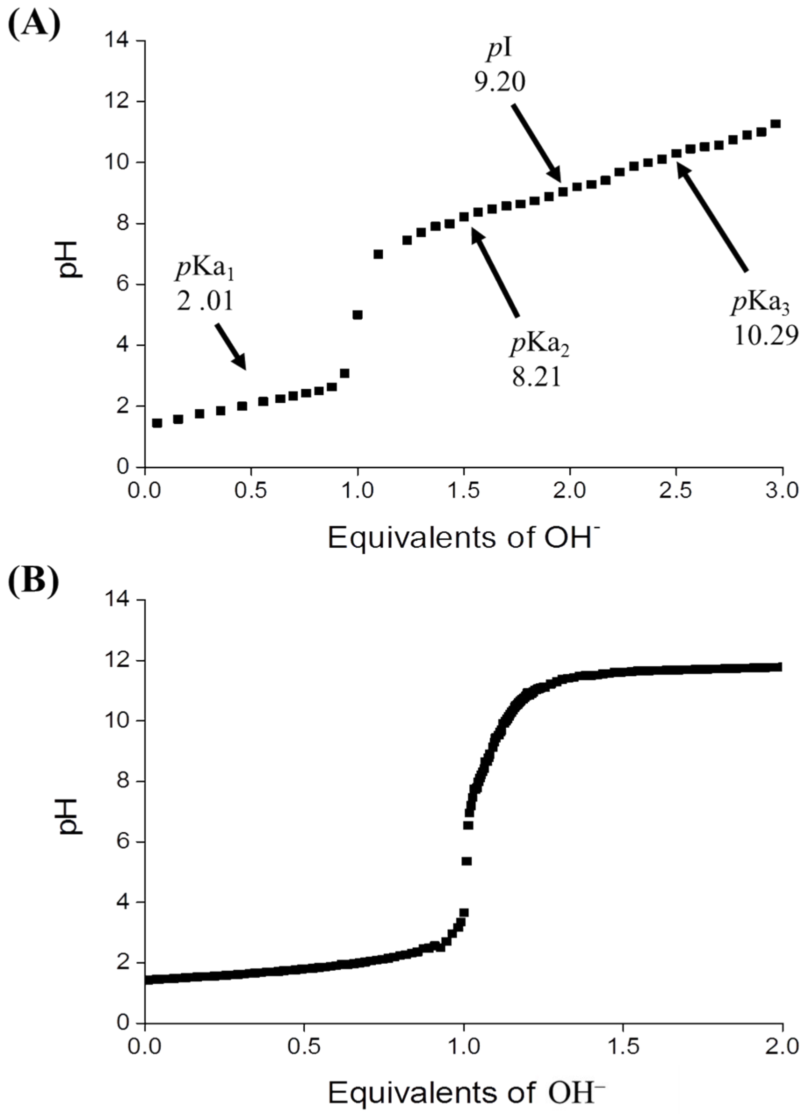


Fig. S4 Potentiometric titration of (A) cysteine (1.4 mM) and (B) as-prepared –[Cys–Au(I)]$_n$– polymers/supramolecules from the reaction of $HAuCl_4$ (1.4 mM) with L-cysteine (1.4 mM) for 1 h. The cysteine or –[Cys–Au(I)]$_n$– polymers/supramolecules are titrated by NaOH (100 mM).

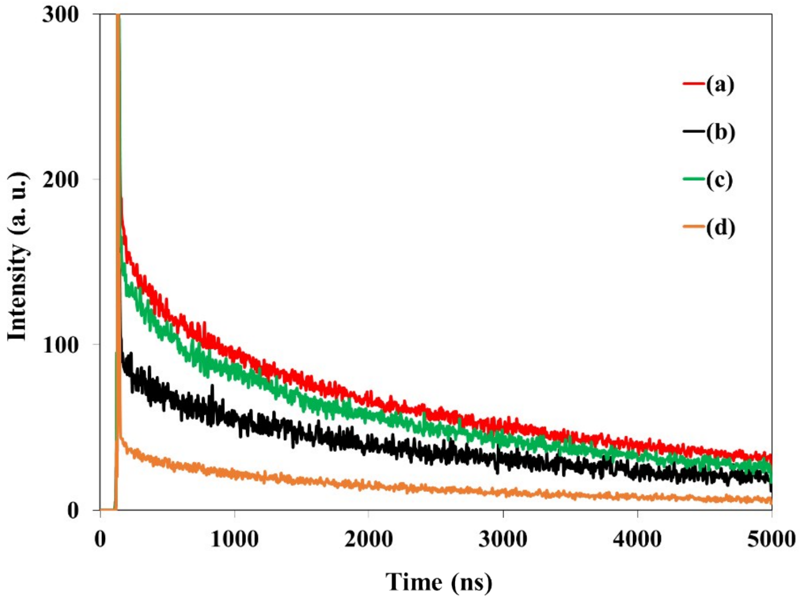


Fig. S5 PL decays of as-prepared (a) Cys–Au NCs_{pH3}, (b) Cys–Au NCs_{pH5}, (c) Cys–Au NCs_{pH7}, and (d) $-[Cys-Au(I)]_n-_{pH9}$ excited with a pulsed laser at 375 nm. Each of them was then fitted to a biexponential PL decay [$I(t) = a_1\exp(-t/\tau_1) + a_2\exp(-t/\tau_2)$], providing lifetimes ($\tau_1/\tau_2$) for the (a) Cys–Au NCs_{pH3}, (b) Cys–Au NCs_{pH5}, (c) Cys–Au NCs_{pH7}, and (d) $-[Cys-Au(I)]_n-_{pH9}$ of 218.68 ns (29.05%)/2288.78 ns (70.95%), 44.27 ns (39.72%)/1876.49 ns (60.28%), 145.07 ns (32.59%)/2190.04 ns (67.41%), and 42.97 ns (63.51%)/1196.65 ns (36.49%), respectively.

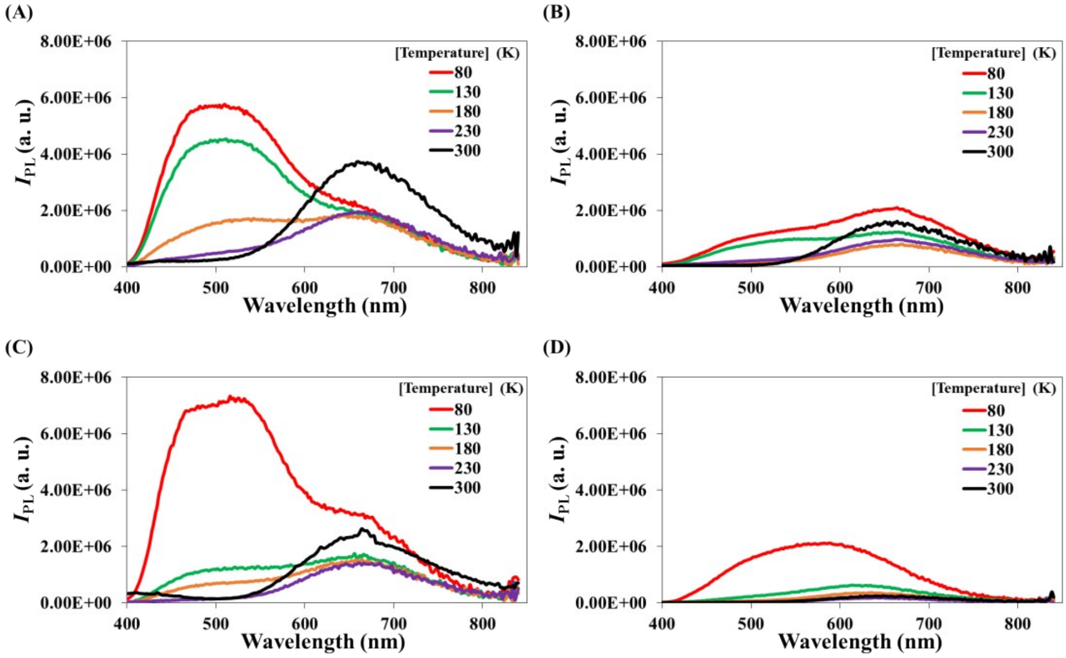


Fig. S6 Temperature-dependent PL spectra of (A) Cys–Au NCs$_{pH3}$-, (B) Cys–Au NCs$_{pH5}$-, and (C) Cys–Au NCs$_{pH7}$-embedded in –[Cys–Au(I)]$_n$– supramolecules and (D) –[Cys–Au(I)]$_n$–$_{pH9}$ at 80–300 K. The PL intensities (I_{PL}) are plotted in arbitrary units (a. u.). Other conditions were the same as those described in Figure 2.

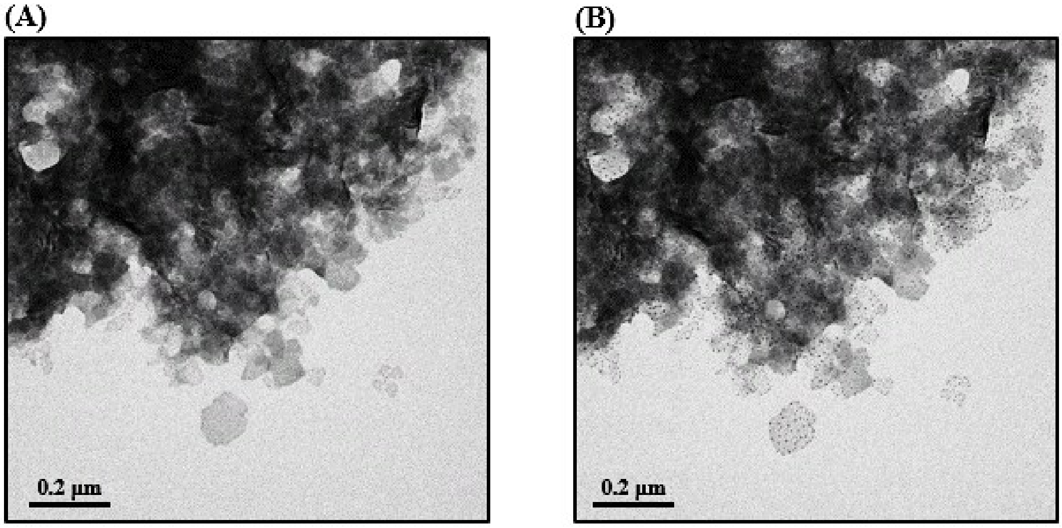


Fig. S7 $-[Cys-Au(I)]_n-$ supramolecules (pH 3) (A) before and (B) after continuous electron-beam irradiation (200 kV) for 10 s during TEM observation.

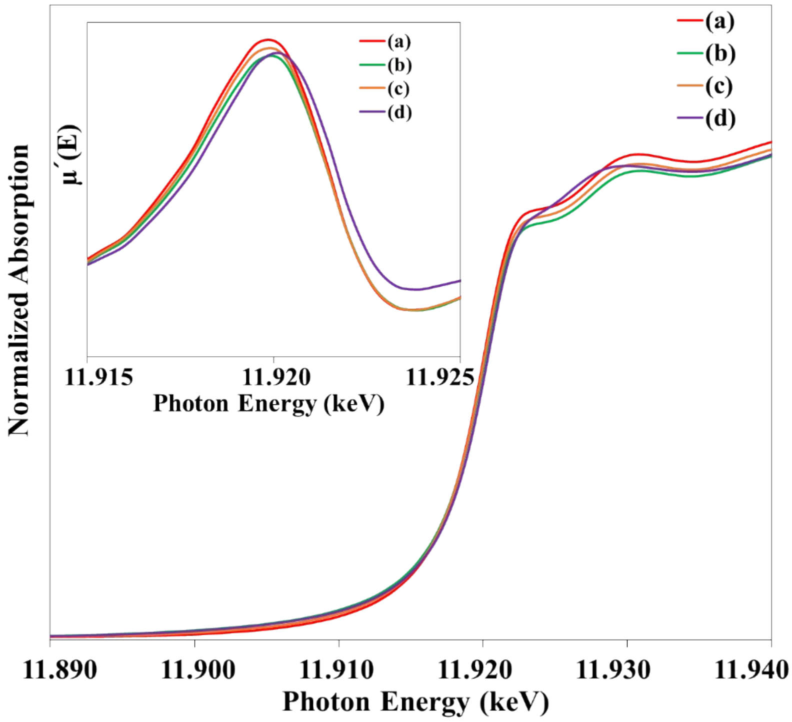


Fig S8 XANES spectra of the Au L_3-edge of as-prepared (a) Cys–Au NCs_{pH3}-, (b) Cys–Au NCs_{pH5}-, and (c) Cys–Au NCs_{pH7}-embedded in –[Cys–Au(I)]$_n$– supramolecules and (d) –[Cys–Au(I)]$_n$–$_{pH9}$. Inset: first-derivative spectra of the corresponding samples.

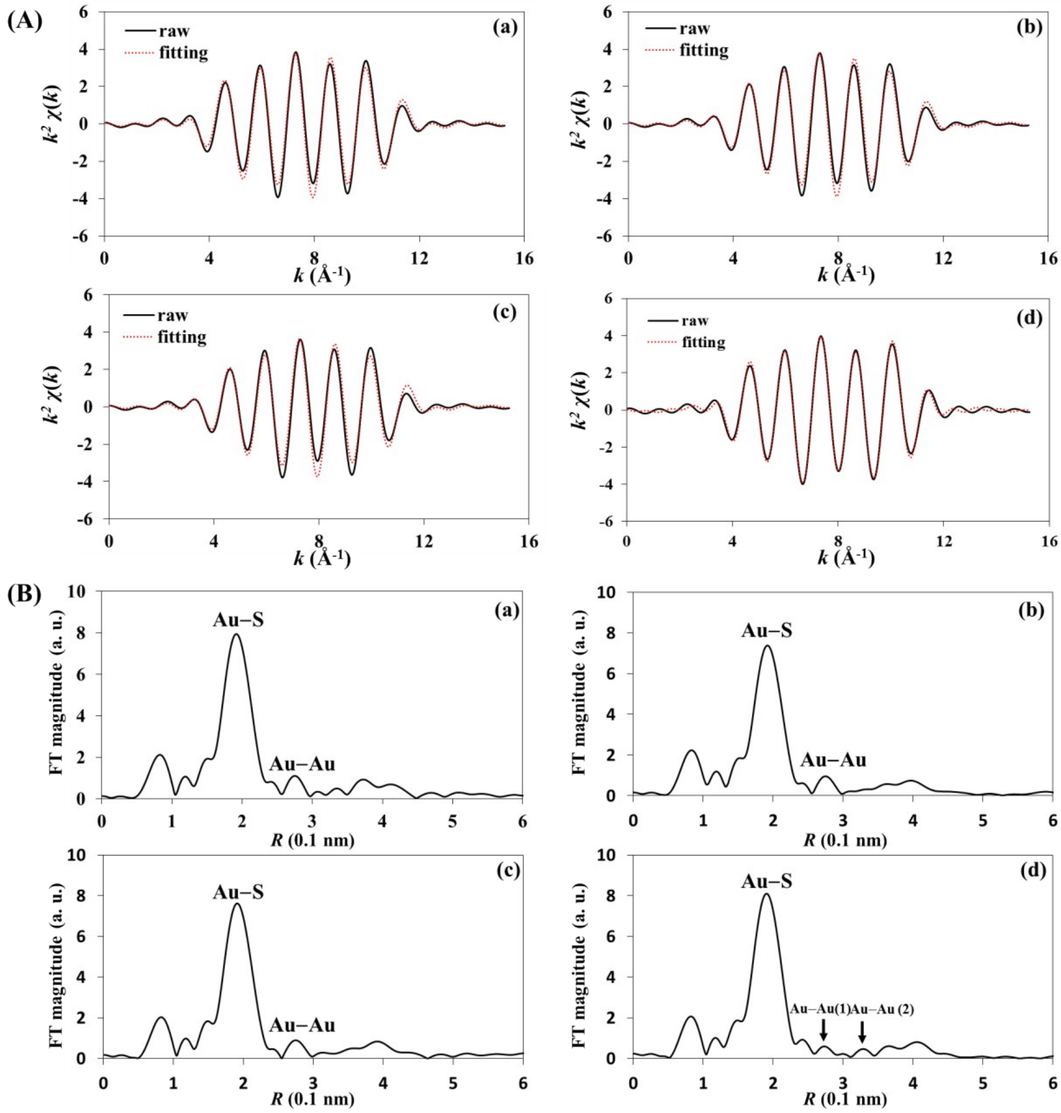


Fig. S9 (A) $k^2\chi(k)$ and the least-squares EXAFS curve-fitting data and (B) Fourier-transformed curves of the $k^2\chi(k)$ functions of the as-prepared (a) Cys–Au NCs_{pH3}-, (b) Cys–Au NCs_{pH5}-, and (c) Cys–Au NCs_{pH7}-embedded in $-[Cys-Au(I)]_n-$ supramolecules and (d) $-[Cys-Au(I)]_n-_{pH9}$.

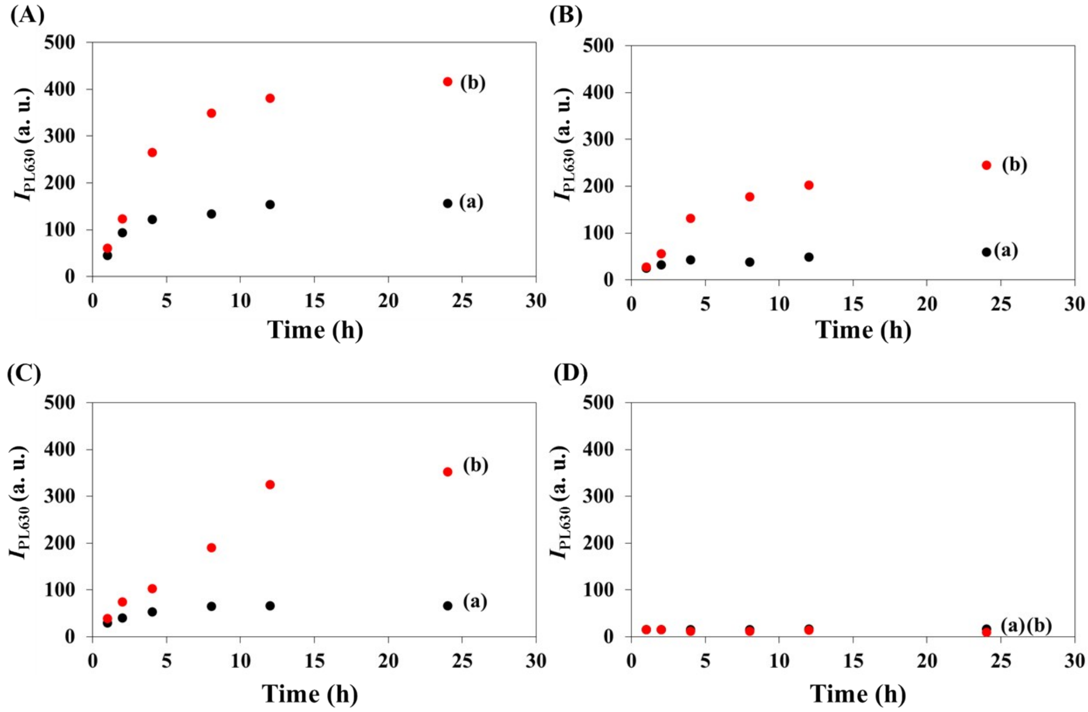


Fig. S10 Time-course measurement of PL intensity at 630 nm (I_{PL630}) for $-$[Cys$-$Au(I)]$_n$$-$ polymers/supramolecules in solutions with pH at (A) 3, (B) 5, (C) 7, and (D) 9 in the (a) absence or (b) presence of $NaBH_4$ (0.75 mM).

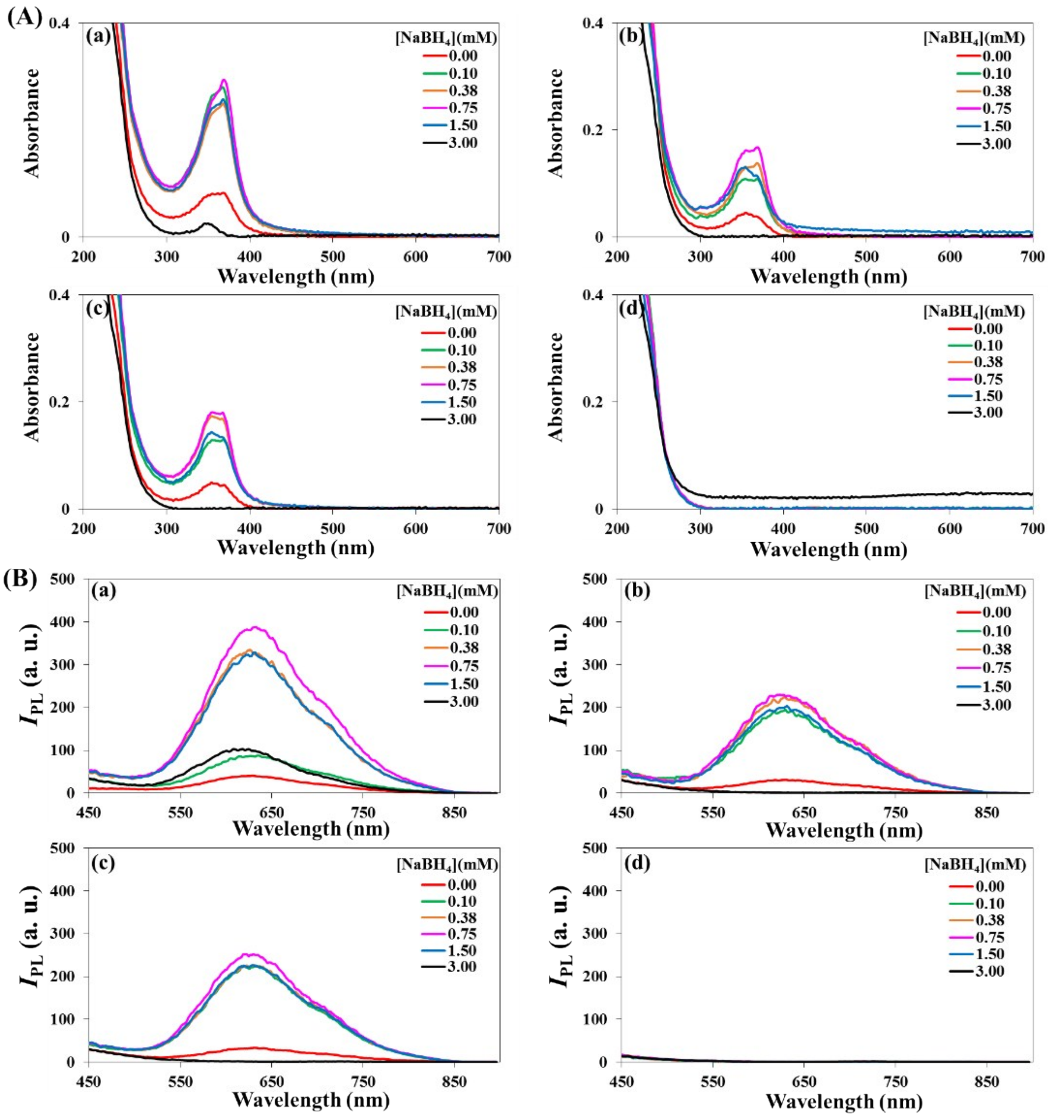


Fig. S11 (A) UV–Vis absorption and (B) PL spectra excited at 365 nm of (a) Cys–Au NCs_{pH3}, (b) Cys–Au NCs_{pH5}, (c) Cys–Au NCs_{pH7}, and (d) $–[Cys–Au(I)]_n–_{pH9}$ synthesized from the reaction of $–[Cys–Au(I)]_n–$ polymers/supramolecules with $NaBH_4$ (0–3.00 mM) for 24 h.

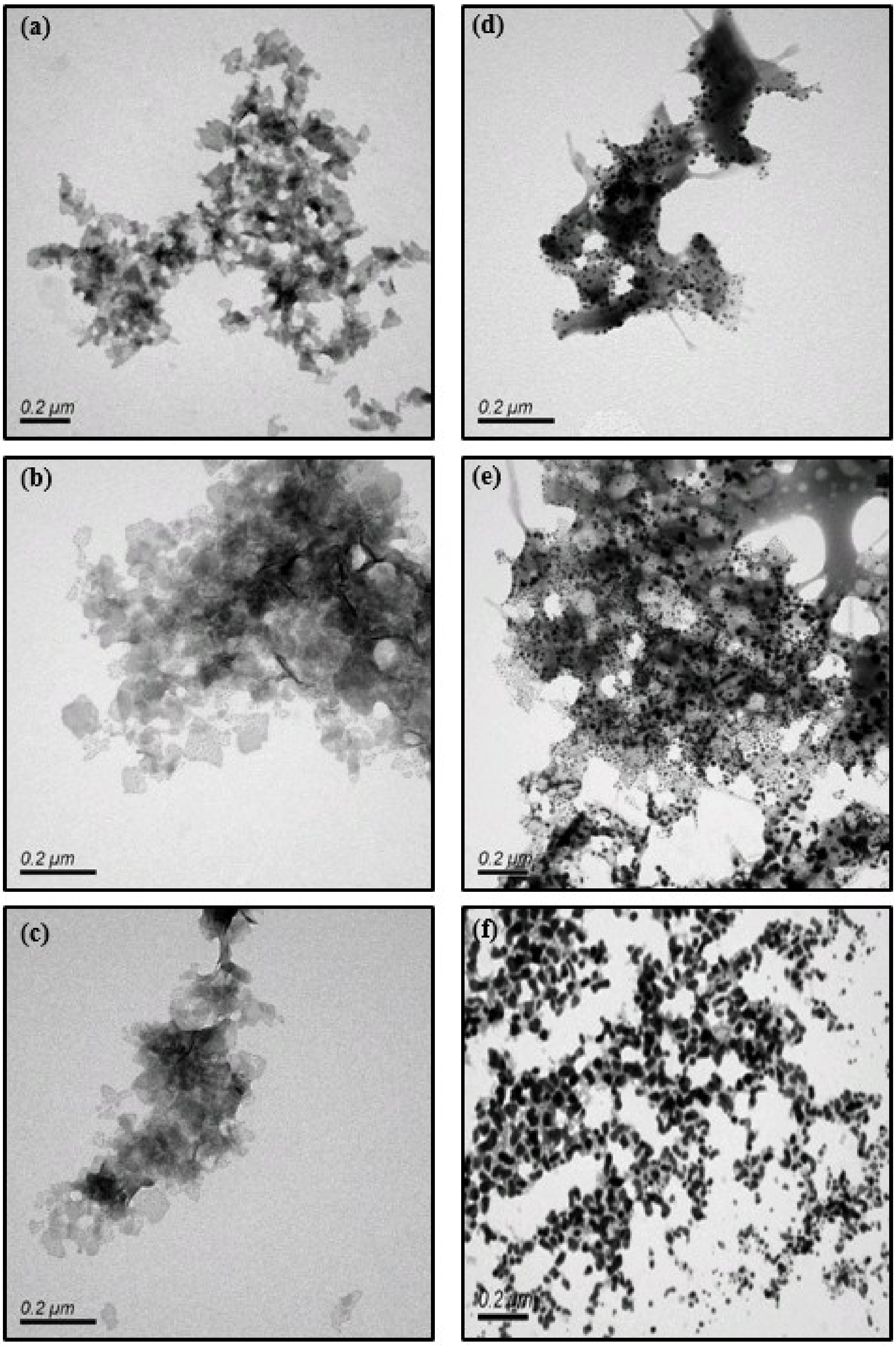


Fig. S12 TEM images of Cys–Au NCs$_{pH3}$/–[Cys–Au(I)]$_n$– supramolecules synthesized from the reactions of –[Cys–Au(I)]$_n$– supramolecules for 24 h with $NaBH_4$ at concentrations of (a) 0 mM, (b) 0.10 mM, (c) 0.38 mM, (d) 0.75 mM, (e) 1.50 mM, and (f) 3.00 mM.

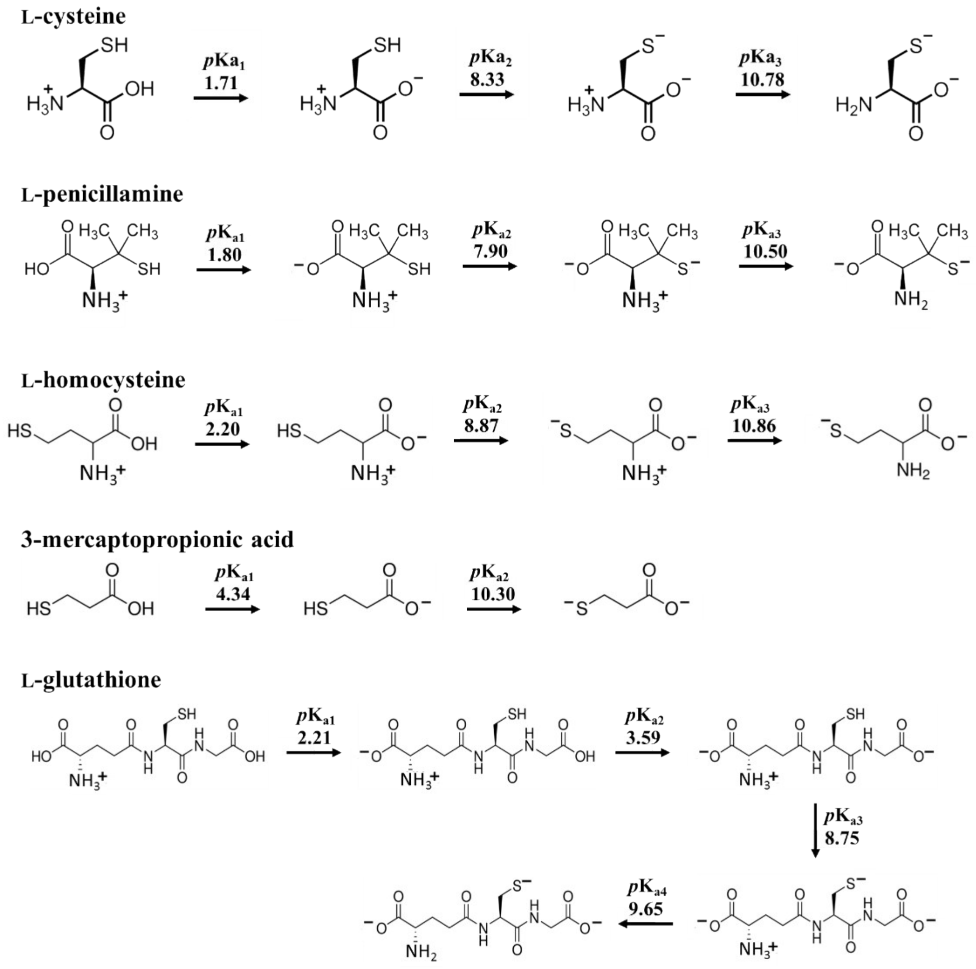


Fig. S13 Structures and ionizations of L-Cys, L-penicillamine, L-homocysteine, 3-mercaptopropionic acid and reduced L-glutathione.

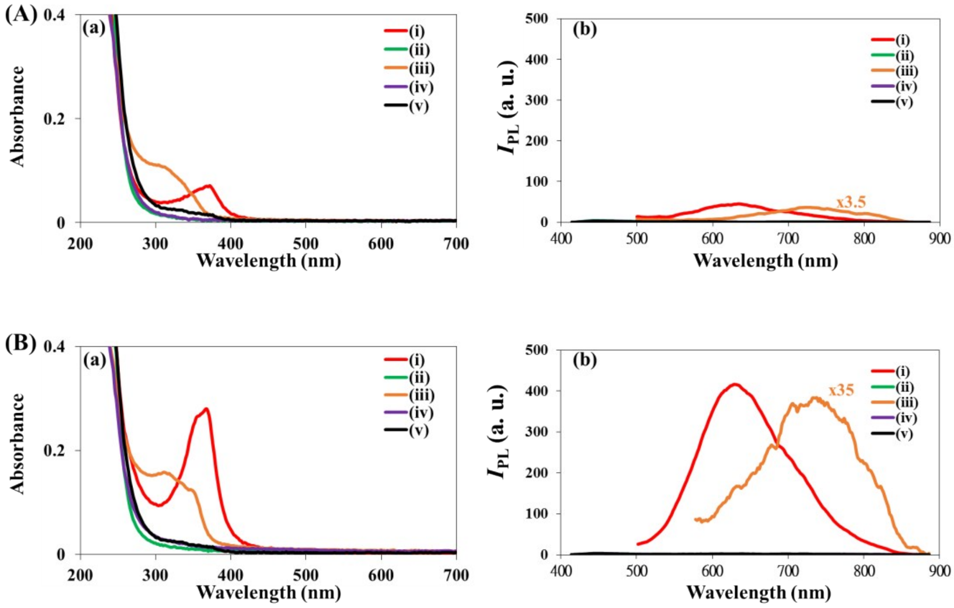


Fig. S14 (a) UV–Vis absorption spectra and (b) PL spectra excited at 365 nm of (i) –[Cys–Au(I)]$_n$–, (ii) –[penicillamine–Au(I)]$_n$– (iii) –[homocysteine–Au(I)]$_n$–, (iv) –[3-mercaptopropionic acid–Au(I)]$_n$–, and (v) –[GSH–Au(I)]$_n$– synthesized in solutions at pH 3 (A) before and (B) after reaction with $NaBH_4$ (0.75 mM) for 24 h. .

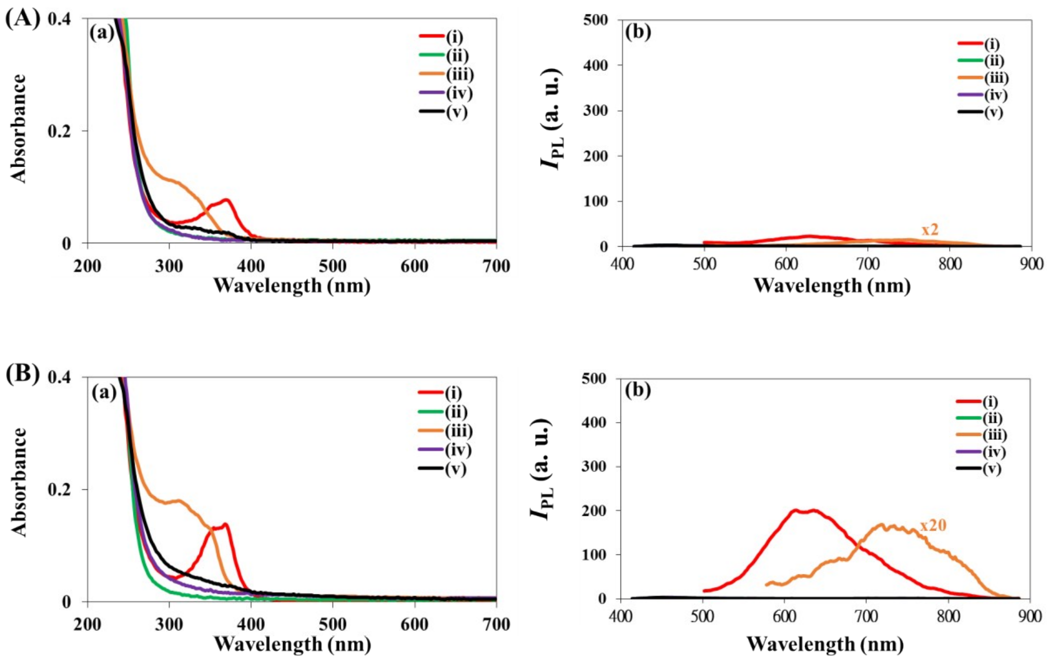


Fig. S15 (a) UV–Vis absorption spectra and (b) PL spectra excited at 365 nm of (i) –[Cys–Au(I)]$_n$–, (ii) –[penicillamine–Au(I)]$_n$– (iii) –[homocysteine–Au(I)]$_n$–, (iv) –[3-mercaptopropionic acid–Au(I)]$_n$–, and (v) –[GSH–Au(I)]$_n$– synthesized in solutions at pH 5: (A) before and (B) after reaction with $NaBH_4$ (0.75 mM) for 24 h.

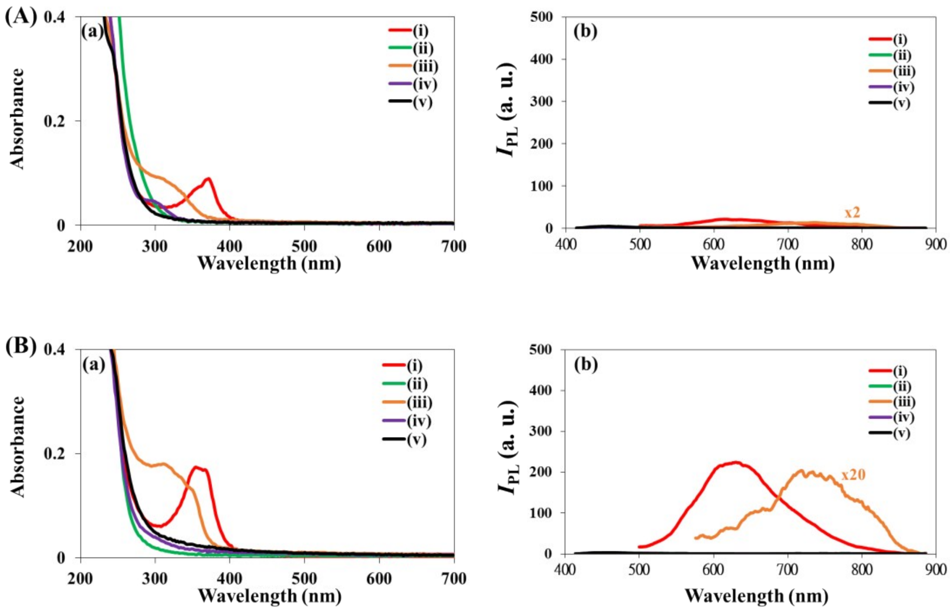


Fig. S16 (a) UV–Vis absorption spectra and (b) PL spectra excited at 365 nm of (i) –[Cys–Au(I)]$_n$–, (ii) –[penicillamine–Au(I)]$_n$– (iii) –[homocysteine–Au(I)]$_n$–, (iv) –[3-mercaptopropionic acid–Au(I)]$_n$–, and (v) –[GSH–Au(I)]$_n$– synthesized in solutions at pH 7: (A) before and (B) after reaction with $NaBH_4$ (0.75 mM) for 24 h.

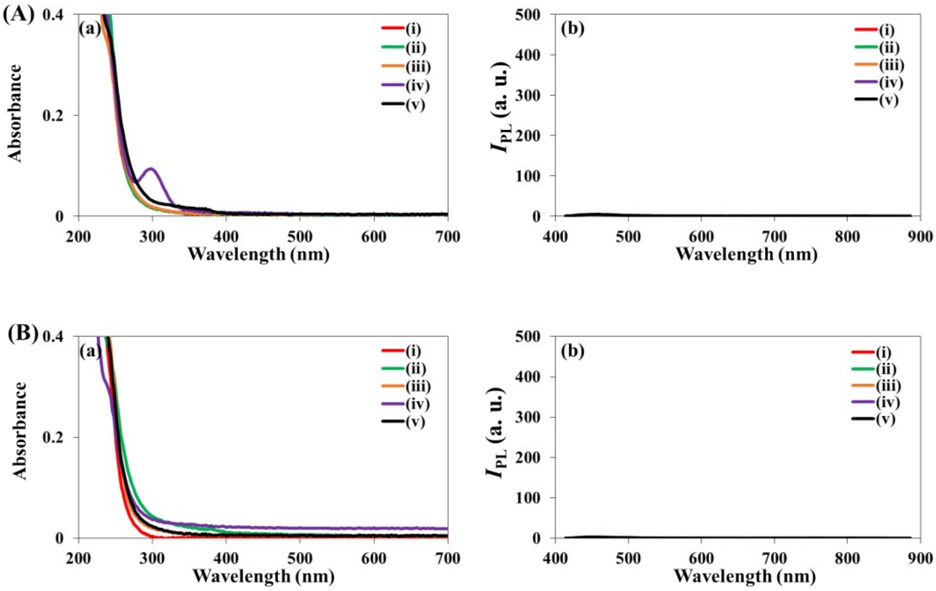


Fig. S17 (a) UV–Vis absorption spectra and (b) PL spectra excited at 365 nm of (i) –[Cys–Au(I)]$_n$–, (ii) –[penicillamine–Au(I)]$_n$– (iii) –[homocysteine–Au(I)]$_n$–, (iv) –[3-mercaptopropionic acid–Au(I)]$_n$–, and (v) –[GSH–Au(I)]$_n$– synthesized in solutions at pH 9: (A) before and (B) after reaction with $NaBH_4$ (0.75 mM) for 24 h.