Electronic Supplementary Information

Highly Fluorescent Hybrid Au/Ag Nanoclusters Stabilized with Poly(ethylene glycol)- and Zwitterion-Modified Thiolate Ligands

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Ligand Synthesis

11-(Acetylthio)undecanoic acid (Compound I). Potassium thioacetate (5.5 g, 0.0564 mol) in one portion to 5.0 g (0.0188 mol) of 11-bromoundecanoic acid in dimethylformamide (100 mL) at ~0 ^{o}C. The mixture was stirred overnight at room temperature, producing dark red solution. Then it was diluted with CH_2Cl_2 (200 mL), and washed three to five times with water. The organic layer was dried over Na_2SO_4, and the solvent was evaporated. The yellow crude product was purified using silica gel column chromatography with chloroform as the eluent. **^{1}H NMR** (600 MHz, in $CDCl_3$): δ (ppm) 2.9 (t, 2H), 2.3-2.4 (5H), 1.6-1.7 (t, 2H), 1.5-1.6 (t, 2H), 1.25-1.4 (m, 12H).

NH_2-PEG_{750}-OCH_3 (Compound IIa) and N_3-PEG_{600}-NH_2 (Compound IIb). Compounds IIa and IIb were synthesized following the procedure reported in the literature.[4,5] To prepare the amine-PEG-methyl ether, the terminal hydroxyl group was first converted to azide group, which was subsequently reduced to amine using triphenylphosphine. For azide-PEG-amine molecule, the

terminal dihydroxy-PEG molecule was first converted to diazide PEG and one azide group was selectively reduced to amine using triphenylphosphine in a two-phase reaction (ethyl acetate/acid water).

Synthesis of AcS-PEG$_{750}$-OCH$_3$ (Compound III). Amounts of 4.66 g (~0.0060 mol) of CH_3O-PEG_{750}-NH_2, 0.1833 g (0.015 mol) of 4-(dimethylamino) pyridine (DMAP), and 1.2 g (0.006 mol) of N,N' -dicyclohexylcarbodiimide (DCC) were added to 40 mL of CH_2Cl_2. An amount of 2.0 g (0.0067 mol) of $AcS(CH_2)_{10}COOH$ dissolved in 20 mL of CH_2Cl_2 was added dropwise to the reaction mixture in an ice bath under N_2. Then the reaction mixture was gradually warmed up to room temperature and further stirred overnight. The mixture was filtered through Celite, and the precipitate was rinsed with CH_2Cl_2. After evaporating solvent, 1 M of HCl was slowly added to the residue. The aqueous mixture was washed three times with ether and saturated by $NaHCO_3$. The product was extracted with CH_2Cl_2 (three times). The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel with CH_2Cl_2 and CH_2Cl_2/MeOH solvents (10:1 v/v) to collect the product. **^{1}H NMR** (600MHz, in $CDCl_3$): δ (ppm) 3.45-3.7 (67 H), 3.4 (s, 3H), 2.8-2.9 (2H), 2.3-2.45 (5H), 1.6-1.7 (2H), 1.5-1.6 (2H), 1.2-1.4 (12H).

Synthesis of AcS-PEG$_{600}$-N$_3$ (Compound IV). $AcS(CH_2)_{10}COOH$ (0.25 g, 0.00096 mol) and CDI (0.195 g, 0.0012 mol) were added in a two-necked flask along with a magnetic stirrer. The flask was purged with N_2 gas and 5 mL of THF was added with a syringe. The mixture was left stirring for 1 hour. Then the mixture was transferred to an addition funnel and added dropwise at 0 ^oC under N_2 to a solution containing 0.51 g (0.0029 mol) of N_3-PEG_{600}-NH_2 in 10 mL of THF. The reaction was continued overnight and the solvent was evaporated. The residue was dissolved in 20 mL of 1M HCl and the product was extracted with ethyl acetate (20 mL, 3 times). The organic layers were combined and washed with saturated $NaHCO_3$ solution and then with water. The organic layer was dried using Na_2SO_4 and the solvent was evaporated. The pure compound was collected by column chromatography using chloroform as solvent. **^{1}H NMR** (600MHz, in $CDCl_3$): δ (ppm) 3.6-3.75 (48H), 3.54 (2H), 3.55 (2H), 3.45 (2H), 3.4 (2H), 2.84 (2H), 2.25-2.4 (4H), 2.2 (2H), 1.5-1.7 (2H), 1.2-1.4 (13H).

Synthesis of AcS-PEG$_{600}$-NH$_2$ (Compound V). Compound IV (1.5 g, ~0.0017 mol) was dissolved in 20 mL of THF in a round bottomed flask equipped with a magnetic stirring bar. Then

triphenylphosphine (0.52 g, 0.002 mol) was added to the solution and left stirring for 3 hours under nitrogen. After 3 hours, 72 μL of DI water was injected into the solution using a syringe and left stirring overnight. Then the solvent was evaporated and the crude product was redissolved in minimum amount of chloroform. The final product was collected by column chromatography using chloroform, methanol and triethylamine (45:45:10) as eluent. **^{1}H NMR** (400 MHz, in $CDCl_3$): δ (ppm) 3.6-3.7 (45H), 3.55-3.6 (4H), 3.45 (4H), 2.9 (2H), 2.35 (3H), 2.15 (2H), 1.5-1.7 (4H), 1.2-1.4 (12H).

Synthesis of AcS-PEG$_{600}$-COOH (Compound VI). Compound V (1.0 g, ~0.0012 mol) was dissolved in 10 mL of chloroform along with succinic anhydride, (0.24 g, 0.0024 mol) and triethylamine (0.42 mL, 0.003 mol). The mixture was stirred overnight under nitrogen. The mixture was poured into HCl solution (30 mL, 1 M) and the product was extracted with chloroform (25 mL, two times). The combined organic layers were dried using Na_2SO_4 and the solvent was dried using a rotary evaporator. **^{1}H NMR** (400MHz, in $CDCl_3$): δ (ppm) 3.6-3.7 (~45H), 3.55 (4H), 3.4 (4H), 2.85 (2H), 2.6-2.7 (2H), 2.5-2.55 (2H), 2.3 (3H), 2.1-2.2 (2H), 1.5-1.7 (4H), 1.2-1.4 (12H).

Coupling of 11-(Acetylthio)undecanoic acid to N,N-dimethyl-1,3-propanediamine (Compound VII). AcS-$(CH_2)_{10}$COOH (0.5 g, 0.00219 mol) and CDI (0.53 g, 0.0033 mol) were added in a two-necked round bottomed flask along with a magnetic stirrer. The flask was purged with N_2 gas and 10 mL of chloroform was added using a syringe. The mixture was left stirring for 1 hour and transferred to an addition funnel and added dropwise under N_2 at 0 ^oC to a three-necked flask containing 1.4 mL of N, N-dimethyl-1,3-propanediamine. After overnight reaction, the mixture was washed with 10% NaCl solution and saturated $NaHCO_3$ solution. The organic layer was then dried using Na_2SO_4 and the solvent was evaporated. The remaining solid product was used as such in the next step.

Synthesis of AcS-zwitterion (Compound VIII). Compound VII (0.53 g, 0.0016 mol) and 1,3-propanesultone (0.58 g, 0.0048 mol) were added in a two-necked round bottomed flask along with a magnetic stirrer. 25 mL of chloroform was added to the flask and the mixture was left stirring under N_2 at room temperature for 2 days. Then chloroform was evaporated to obtain a pale residue.

The residue was then washed several times with THF to remove excess of unreacted sultone. The solid product was dried under vacuum.

Deprotection of the thiol group. To convert the acetyl group protected thiol to free thiol, 0.5 g of the ligand was dissolved in 5 mL of methanol, 1 equivalent of NaOH dissolved in 1 mL of water was injected into the solution and the mixture was left stirring for 24 hours under N_2. The product was neutralized by adding HCl (a few mL of 0.5 M solution). After evaporation of methanol, the PEG ligands were extracted in DCM or ethyl acetate and the pure product was obtained by evaporating the solvent. To collect monothiol-zwitterion ligand, methanol was first evaporated. Then the ligand was precipitated using THF. The precipitate was dried under vacuum and re-dispersed in methanol. The insoluble salts were precipitated out and the clear supernatant liquid was collected. The solvent was evaporated again and the dissolution-precipitation was repeated two times.

HS-PEG$_{750}$-OCH$_3$ (compound IIIb). **^{1}H NMR** (600MHz, in $CDCl_3$): δ (ppm) 3.45-3.7 (64 H), 3.4 (s, 3H), 2.7 (1H), 2.5-2.55 (1H), 2.2-2.3 (2H), 1.5-1.7 (4H), 1.2-1.4 (12H).

HS-PEG$_{600}$-N$_3$ (compound IVb). **^{1}H NMR** (600MHz, in $CDCl_3$): δ (ppm) 3.5-3.75 (48H), 3.45 (2H), 3.4 (2H), 2.6 (2H), 2.2 (2H), 1.55-1.7 (4H), 1.2-1.4 (13H).

HS-PEG$_{600}$-NH$_2$ (compound Vb). **^{1}H NMR** (400MHz, in $CDCl_3$): δ (ppm) 3.5-3.7 (~46H), 3.55 (4H), 3.45 (4H), 2.65 (2H), 2.15 (2H), 1.55-1.7 (4H), 1.2-1.4 (13H).

HS-PEG$_{600}$-COOH (compound VIb). **^{1}H NMR** (400MHz, in $CDCl_3$): δ (ppm) 3.5-3.7 (~46H), 3.45-3.55 (4H), 3.35-3.45 (4H), 2.6 (2H), 2.4 (2H), 2.15 (2H), 1.5-1.65 (4H), 1.2-1.4 (12H).

HS-(CH$_2$)$_{10}$-zwitterion (compound VIIIb). **^{1}H NMR** (600MHz, in D_2O): δ (ppm) 3.35-3.45 (2H), 3.2-3.35 (2H), 3.15-3.25 (2H), 2.95-3.05 (6H), 2.8-2.9 (2H), 2.35-2.6 (2H), 2.05-2.2 (4H), 1.8-2 (2H), 1.1-1.35 (12H).

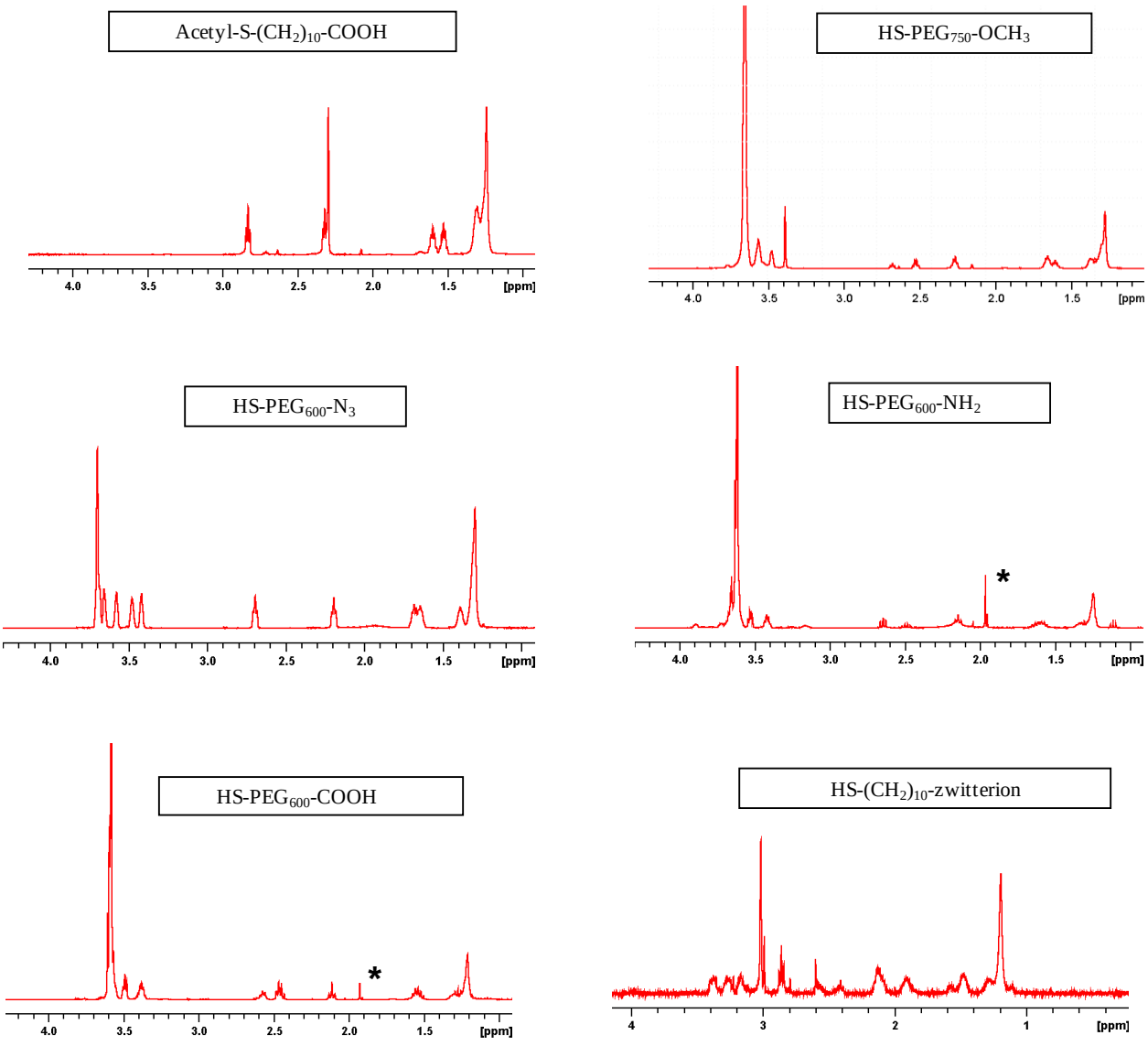

Figure S1. NMR spectra of the acetyl protected mercaptoundecanoic acid along with monothiol PEG and zwitterion ligands. The spectra of PEGylated ligands were recorded in $CDCl_3$ while the spectrum of the ligand modified with a zwitterion group was recorded in D_2O.

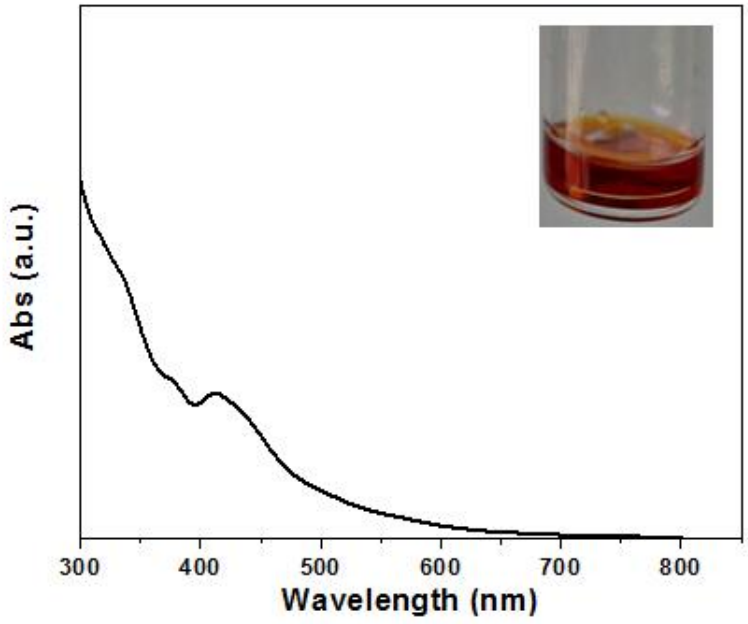

Figure S2. Optical absorption of the as prepared $[Au_{11}(PPh_3)_8Cl_2]^+$ clusters in ethanol. Inset shows a white light image of the cluster solution.

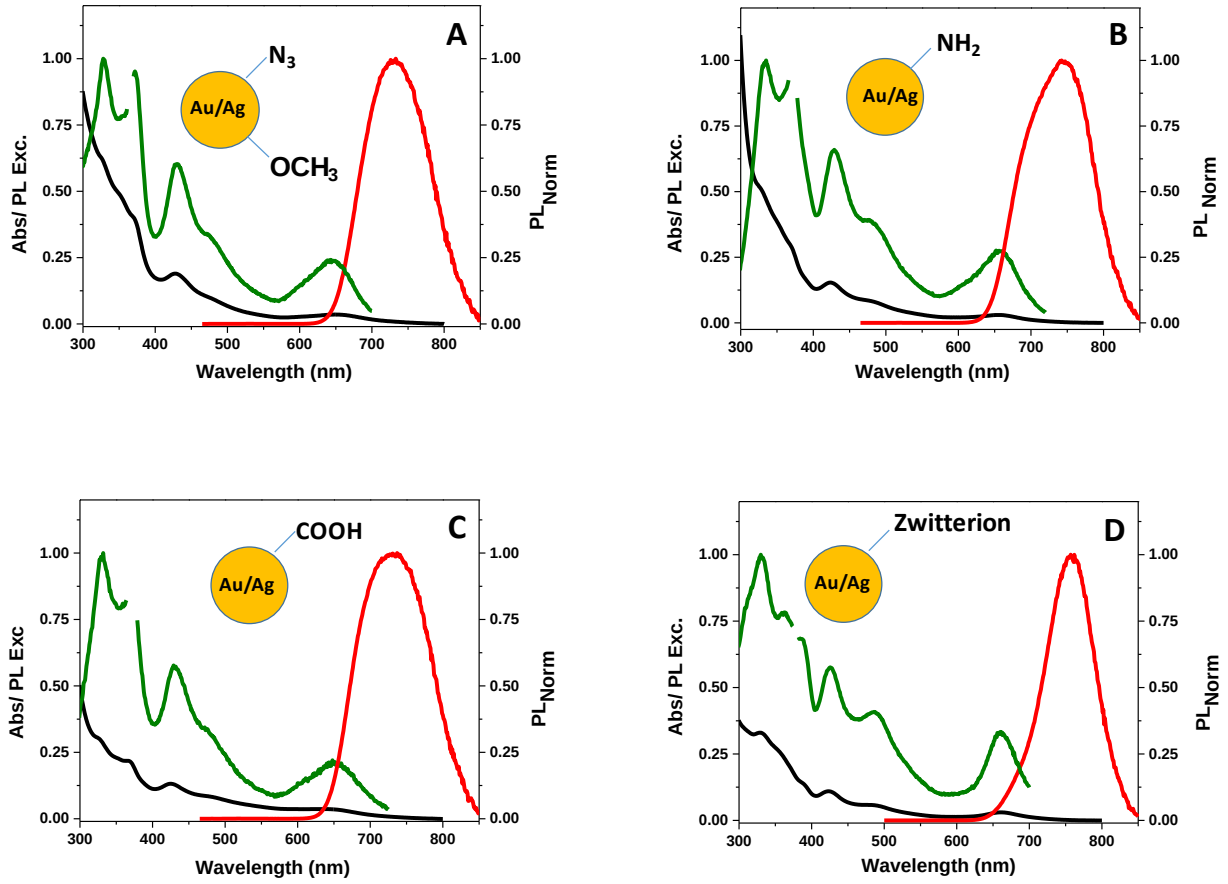

Figure S3. Optical absorption (black line), PL excitation (green line) and PL emission (red line) spectra collected from dispersions of nanoclusters protected by: (A) thiol-PEG_{600}-N_3/thiol-PEG_{750}-OCH_3 (1:1), (B) thiol-PEG_{600}-NH_2, (C) thiol-PEG_{600}-COOH and (D) thiol-zwitterion.

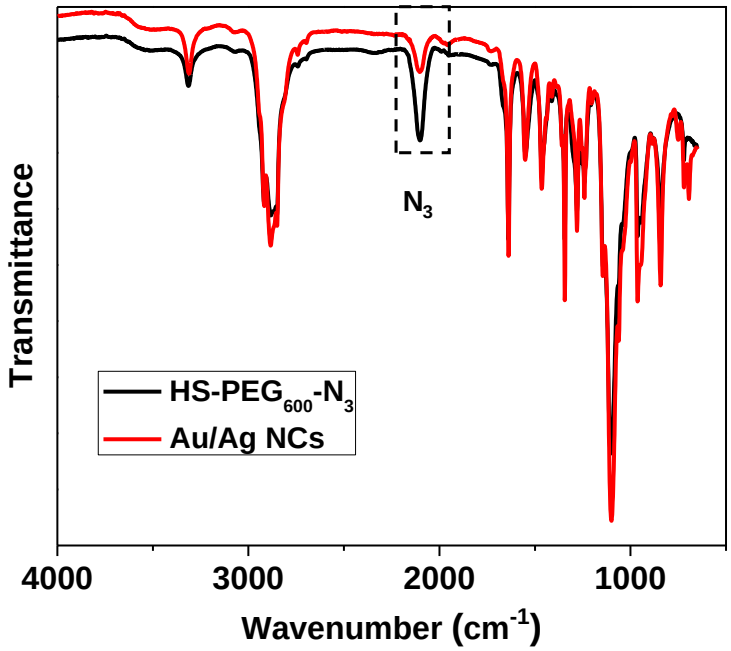

Figure S4. FT-IR spectra collected from the thiol-PEG_{600}-N_3 ligand alone and Au/Ag nanoclusters capped with 50:50 mixture of N_3- and OCH_3-functionalized PEG-thiolate ligands. The azide signature is boxed.

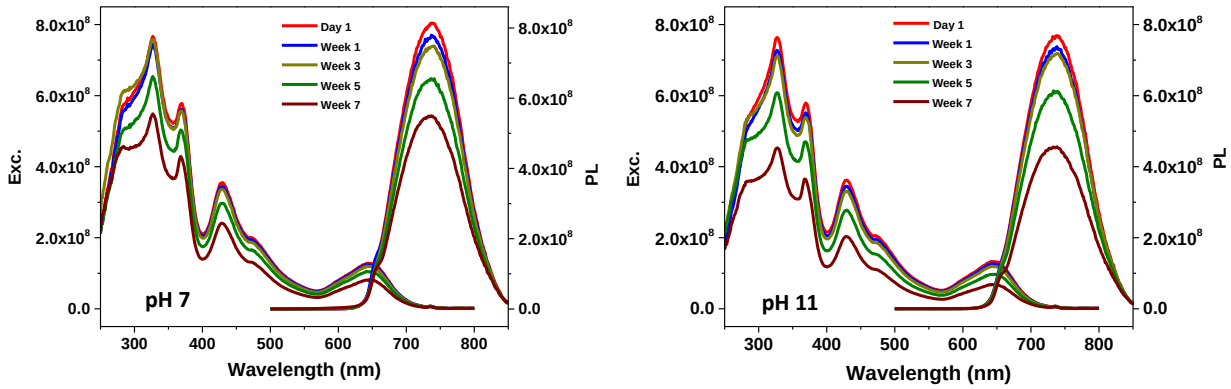

Figure S5. PL excitation and emission spectra collected from methoxy-PEG-thiol-capped NCs in pH 7 and pH 11 buffer solutions collected from freshly prepared samples and after 1, 3, 5 and 7 weeks of storage.