Supporting Information for

Unique Ultrafast Visible Luminescence in Monolayer-Protected Au_{25} Clusters

[a]*Mary Sajini Devadas,* [a]*Junhyung Kim,* [a]*Ekkehard Sinn,* [b]*Dongil Lee,* [c]*Theodore Goodson III and* [a]*Guda Ramakrishna*[*]

[a]Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008

[b]Department of Chemistry, Yonsei University, Seoul 120-749, Korea

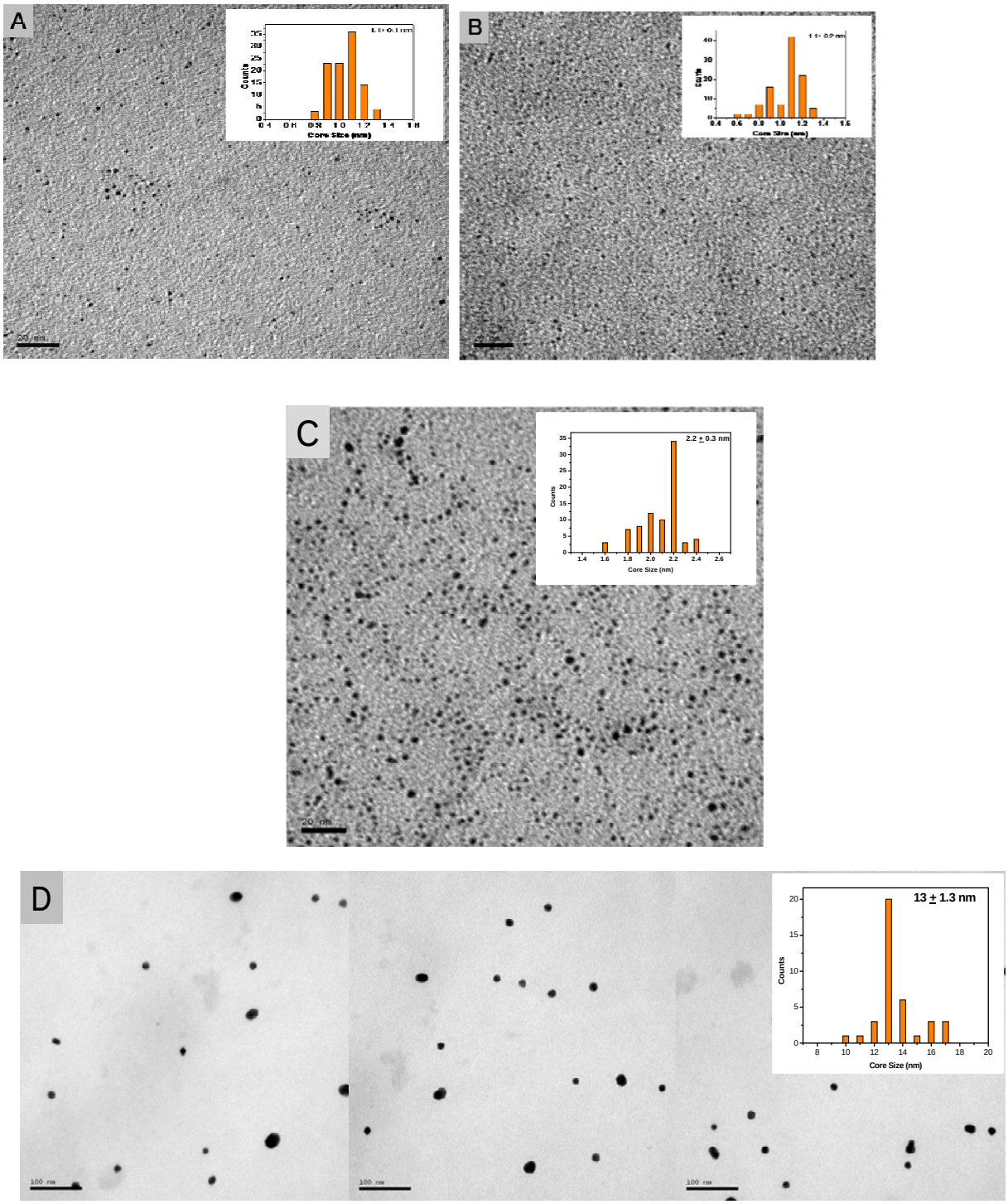
[c]Department of Chemistry, University of Michigan, Ann Arbor MI 48109

E-mail: rama.guda@wmich.edu

1. Transmission Electron Microscopy (TEM) measurements

TEM images of MPC samples were obtained with a JEOL transmission electron microscope (JEM-1230). MPC samples were prepared by dipping a Formvar/carbon-coated copper grid (400C-FC, EMS) in 1 mg/mL MPC in CH_2Cl_2 for the hexanethiolate MPC and water in the case of the glutathione MPC and citrate nanoparticle. Three typical regions of each sample were imaged at 600 K magnification and 200 K magnification for the Au-Citrate sample. Core-size histograms were read from digitized photographic images using ImageJ software [*http://rsb.info.nih.gov/ij/*].

Values were confirmed by manual reading. Shown in Figure S1 are the TEM images of $Au_{25}(C_6S)_{18}$, $Au_{25}(GS)_{18}$, 2.2 nm-Au(GS), and 13 nm-Au(Cit) and the insert shows the histogram of sizes.



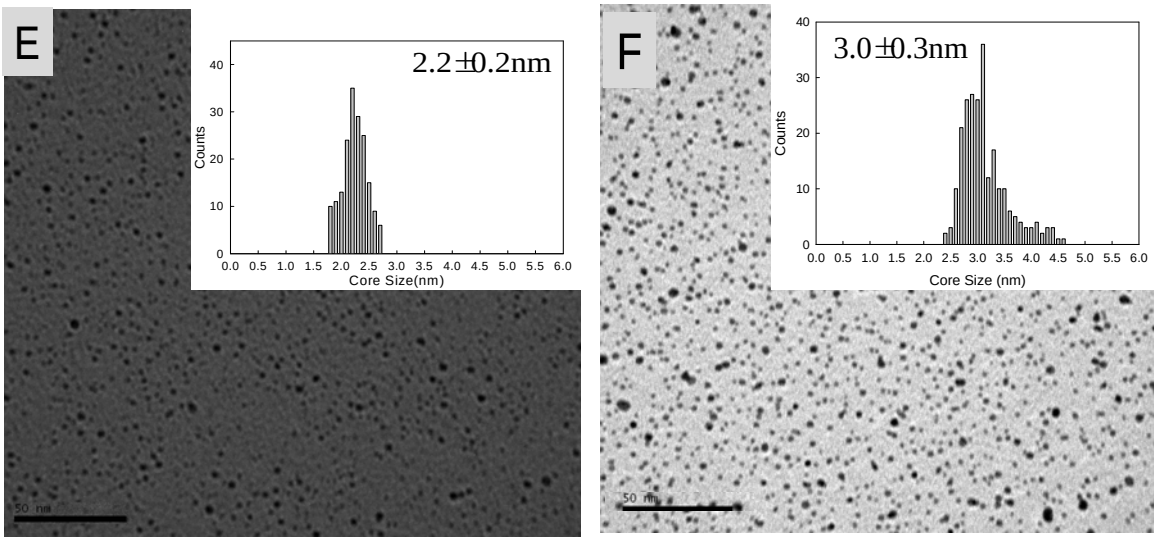


Figure S1: TEM image of the synthesized (A) $Au_{25}(C_6S)_{18}$ clusters (B) $Au_{25}(GS_{18}$ (C) 2.2 nm-Au(GS), (D) 13 nm-Au(Cit) , (E) 2.2 nm- Au(C_6S) and (F) 3 nm-Au(C_6S) and the insert shows the histogram of sizes. Scale bars are 20 nm for A, B, C, 100 nm for D and 50 nm for E and F respectively.

2 Electrochemical measurements

Voltammetry was carried out on an electrochemical workstation (Model 660B, CH instruments) in 0.1 M Bu_4NClO_4 in CH_2Cl_2 solutions that were degassed with high-purity Ar gas. The working electrode was a 0.4 mm Pt disk, the counter electrode was a 0.4 mm Pt disk, and the reference electrode was a silver wire quasi-reference electrode. Square wave voltammetry (SWV) was carried out with potential steps of 4 mV, square wave amplitude of 25 mV, square wave frequency of 15 s^{-1}, and a quiet time of 5 s.

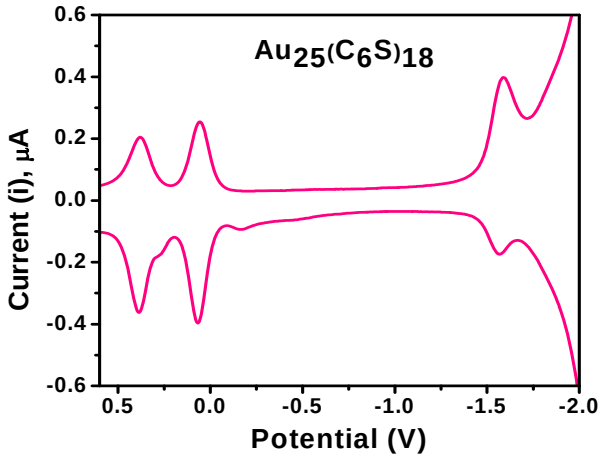


Figure S2: Square Wave Voltammogram of $Au_{25}(C_6S)_{18}$ clusters.

3. Luminescence decay analyses

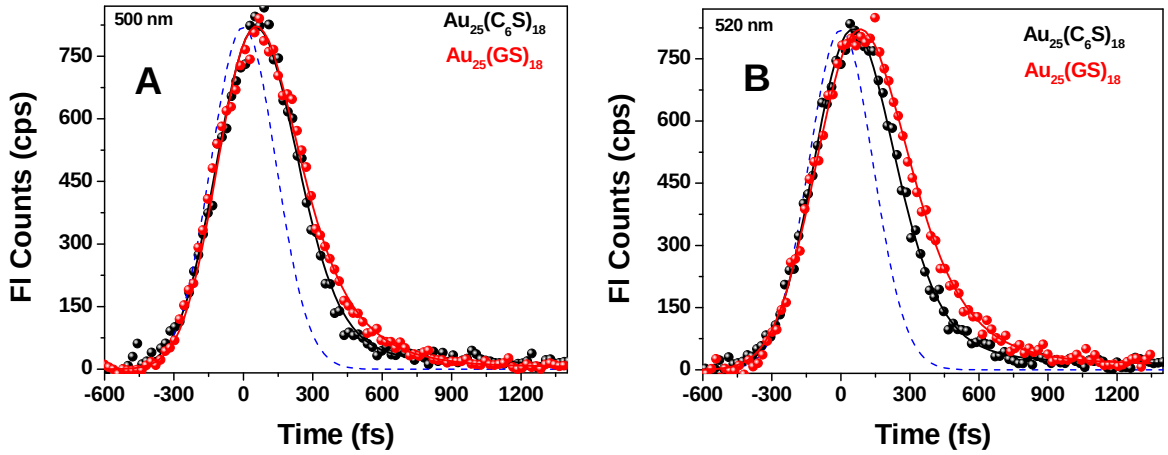
Obtained luminescence kinetics of $Au_{25}L_{18}$ clusters are fitted with exponential growth and kinetics given in the equations 1 and 2 of the manuscript and the time constants are provided in Table S1.

Table S1: Lifetimes of Au_{25} clusters capped with hexanethiol and glutathione at different emission wavelengths after excitation at 400 nm

Sample/wavelength	τ_g	τ_1	τ_2	$\tau_{d,\,av}$ **(fs)**
$Au_{25}(C_6S)_{18}$/500 nm	180 fs	200 fs (99.8%)	1.65 ps (0.2%)	200
$Au_{25}(C_6S)_{18}$/520 nm	200 fs	230 fs (99.8%)	1.05 ps (0.2%)	230
$Au_{25}(C_6S)_{18}$/550 nm	220 fs	280 fs (99.4%)	1.65 ps (0.6%)	290
$Au_{25}(C_6S)_{18}$/580 nm	230 fs	310 fs (98.6%)	1.65 ps (1.4%)	330
$Au_{25}(C_6S_{18}$/610 nm	235 fs	350 fs (96.1%)	2.2 ps (3.9%)	420
$Au_{25}(C_6S)_{18}$/640 nm	245 fs	420 fs (97.3%)	1.5 ps (2.7%)	450
$Au_{25}(C_6S)_{18}$/670 nm	300 fs	570 fs (93.5%)	6.8 ps (6.5%)	980
$Au_{25}(GS)_{18}$/480 nm	140 fs	185 fs (99.9%)	1.6 ps (0.1%)	185
$Au_{25}(GS)_{18}$/500 nm	180 fs	230 fs (99.5%)	1.6 ps (0.5%)	240

$Au_{25}(GS)_{18}$/520 nm	210 fs	270 fs (99.3%)	1.6 ps (0.7%)	280
$Au_{25}(GS)_{18}$/550 nm	220 fs	290 fs (97.6%)	1.65 ps (2.4%)	320
$Au_{25}(GS)_{18}$/580 nm	220 fs	340 fs (95.9%)	2.8 ps (4.1%)	440
$Au_{25}(GS)_{18}$/610 nm	235 fs	330 fs (90.1%)	2.1 ps (9.9%)	505
$Au_{25}(GS)_{18}$/640 nm	250 fs	410 fs (84.2%)	4.8 ps (15.8%)	1100
$Au_{25}(GS)_{18}$/670 nm	300 fs	525 fs (68.7%)	3.6 ps (26.9%), >10 ps (4.4%)	1400

Luminescence traces obtained for gold clusters, $Au_{25}(C_6S)_{18}$ in DCM and $Au_{25}(GS)_{18}$ in water at different luminescence wavelengths are shown in parts A, B, C, D, E and F of Figure S3. It can be observed that the growth of the emission is independent of the ligand while the decay of fluorescence is varied with passivating ligand. Slower decay is observed for the GS capping ligand over C_6S.



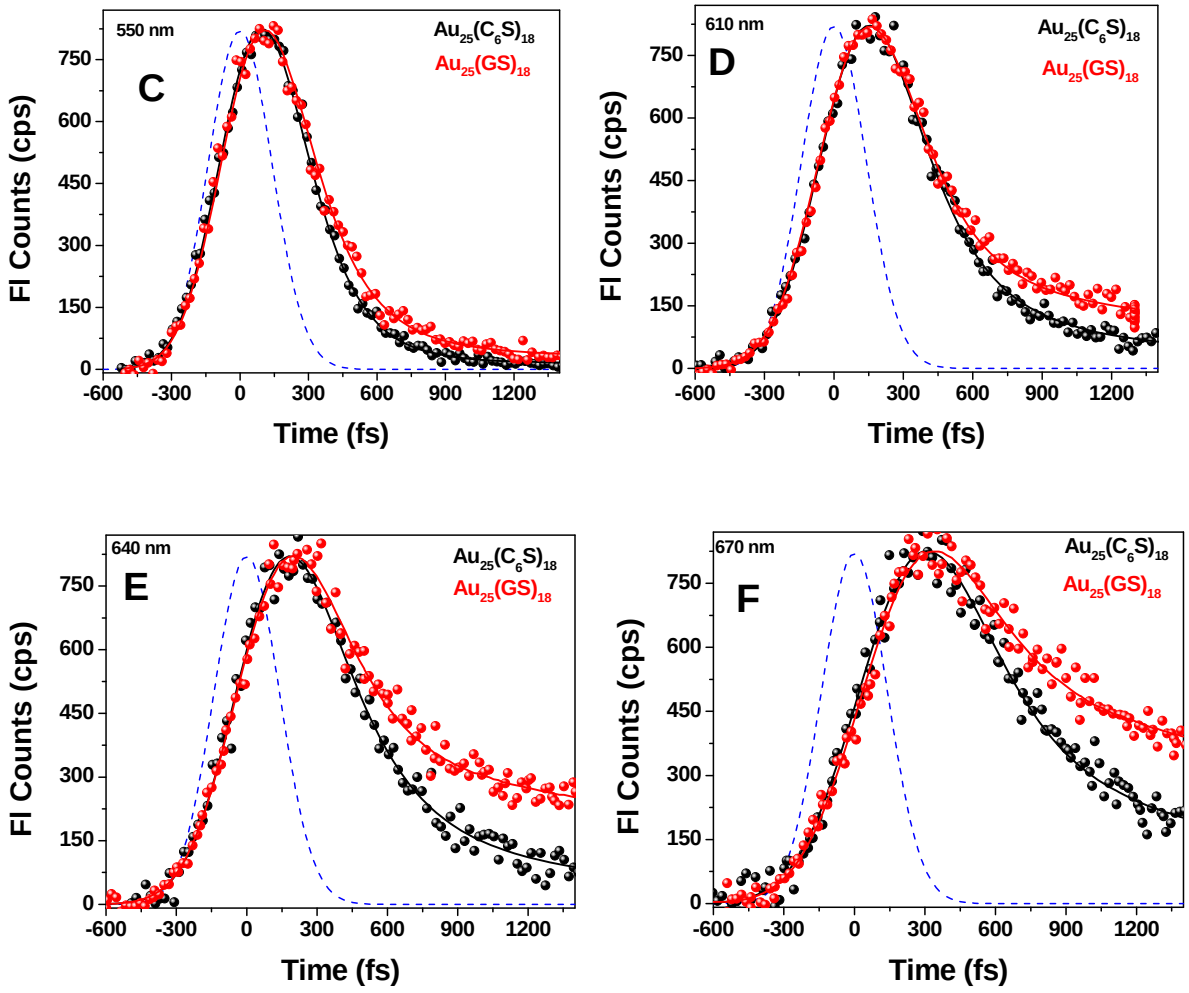


Figure S3: Comparative luminescence decay traces for $Au_{25}(C_6S)_{18}$ in DCM and $Au_{25}(GS)_{18}$ in water at the monitoring wavelengths of (A) 500 nm, (B) 520 nm, (C) 550 nm, (D) 610 nm, (E) 640 nm and (F) 670 nm after excitation at 400 nm.