Supporting Information

Ultrabright Luminescence from Gold Nanoclusters: Rigidifying the Au(I)-Thiolate Shell

Kyunglim Pyo[a†], Viraj Dhanushka Thanthirige[b†], Kyuju Kwak[a], Prabhu Pandurangan[a], Guda Ramakrishna[b] and Dongil Lee[a]**

[a]Department of Chemistry, Yonsei University, Korea

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

[†] These authors contributed equally to this study.

[*] E-mail: dongil@yonsei.ac.kr, rama.guda@wmich.edu

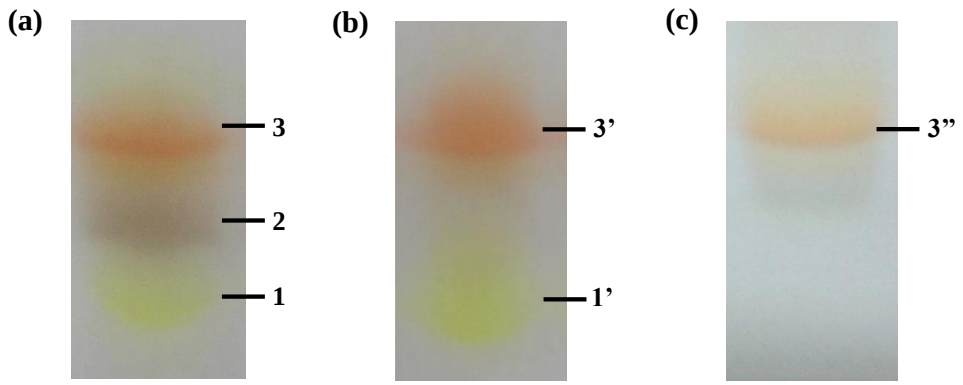

Figure S1. PAGE analysis of the reaction product. After (a) 2h- (b) 6h-stirring and (c) separation using water-IPA mixture solvent fractionation. The bands 1 and 1′ were identified as $Au_{15}(SG)_{13}$, the band 2 was identified as $Au_{18}(SG)_{14}$ and the bands 3, 3′, and 3″ were identified as $Au_{22}(SG)_{18}$.

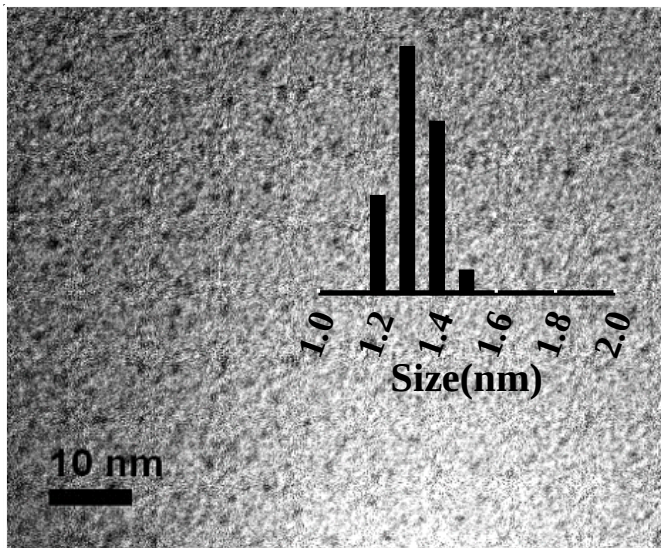

Figure S2. TEM image of the isolated $Au_{22}(SG)_{18}$. The average size of the clusters was 1.3 ± 0.3 nm.

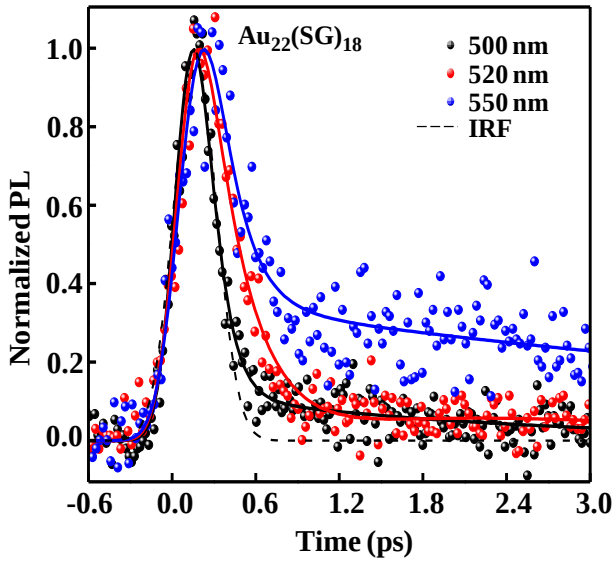

Figure S3. Femtosecond luminescence decay traces at visible wavelength regions after excitation at 400 nm. Also, shown in the figure is the instrument response function obtained from Raman scattering of water.

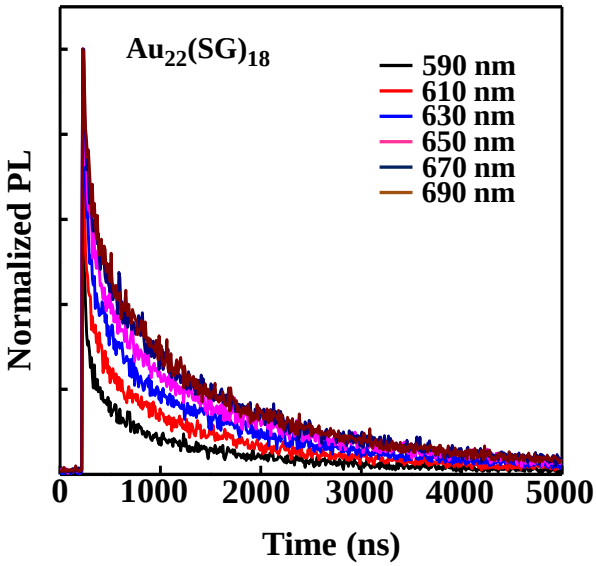

Figure S4. Nanosecond time-resolved luminescence decay traces obtained from time-correlated single photon counting technique after excitation at 503 nm.

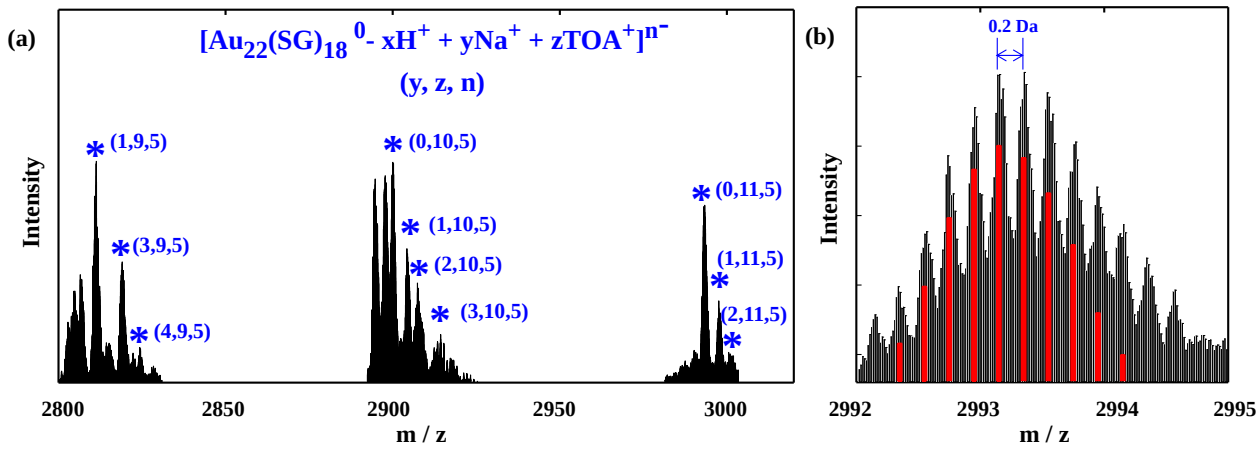

Figure S5. (a) Negative-mode ESI mass spectrum of TOA-Au_{22}. The assignment coding x, y, z, and n in parenthesis represent, respectively, the number of dissociated H^+, paired Na^+ and TOA^+ ions, and charge of cluster anions. (x = y + z + n) (b) A comparison between the experimental data (black line) and the calculated isotope pattern (red line) of $[Au_{22}(SG)_{18}{}^0 - 16H^+ + 11TOA^+]^{5-}$.

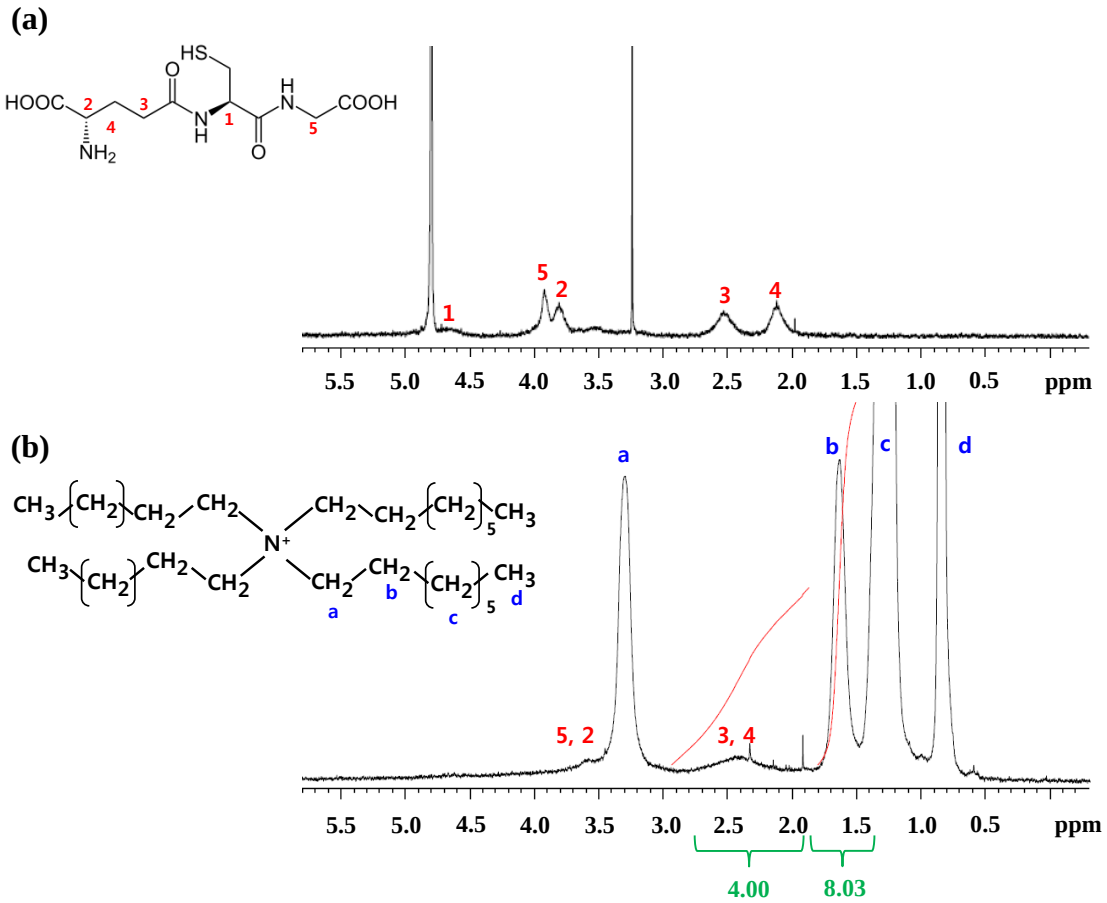

Figure S6. ^1H NMR spectra of (a) $Au_{22}(SG)_{18}$ in D_2O and (b) TOA-Au_{22} in chloroform. For TOA-Au_{22}, the number of TOA bound to $Au_{22}(SG)_{18}$ was determined to be ~18 by comparing the intensity of the ^1H NMR resonance for **3+4** (2.0-2.7 ppm) and **b** (1.5-1.8 ppm).

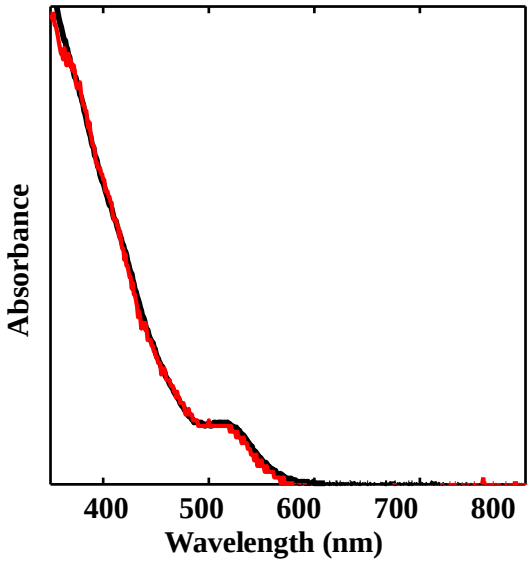

Figure S7. UV-vis absorption spectra of $Au_{22}(SG)_{18}$ in water (black) and TOA-Au_{22} in toluene (red). Both solutions were the same $Au_{22}(SG)_{18}$ concentration of 1.1 mM.

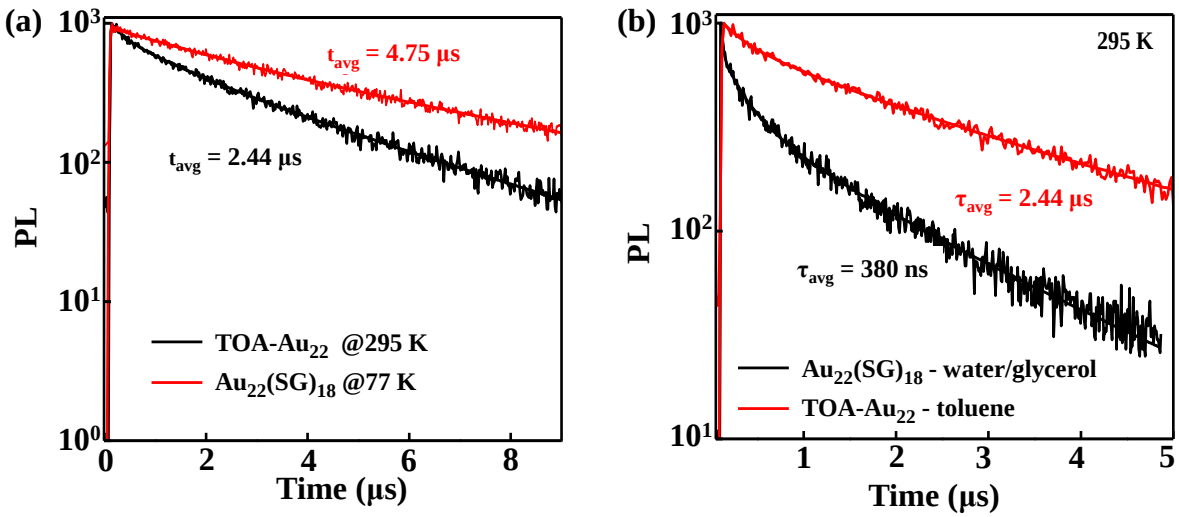

Figure S8. Comparison of Luminescence Lifetime of $Au_{22}(SG)_{18}$ and TOA-Au_{22}. (a) Luminescence decay comparison of TOA-Au_{22} at 295 K with $Au_{22}(SG)_{18}$ at 77 K. (b) Comparison of luminescence decay traces of TOA-Au_{22} and $Au_{22}(SG)_{18}$ at 295 K. The differences are obvious with more than 6-fold longer lifetime for TOA-Au_{22} compared to that of $Au_{22}(SG)_{18}$ at 295 K.

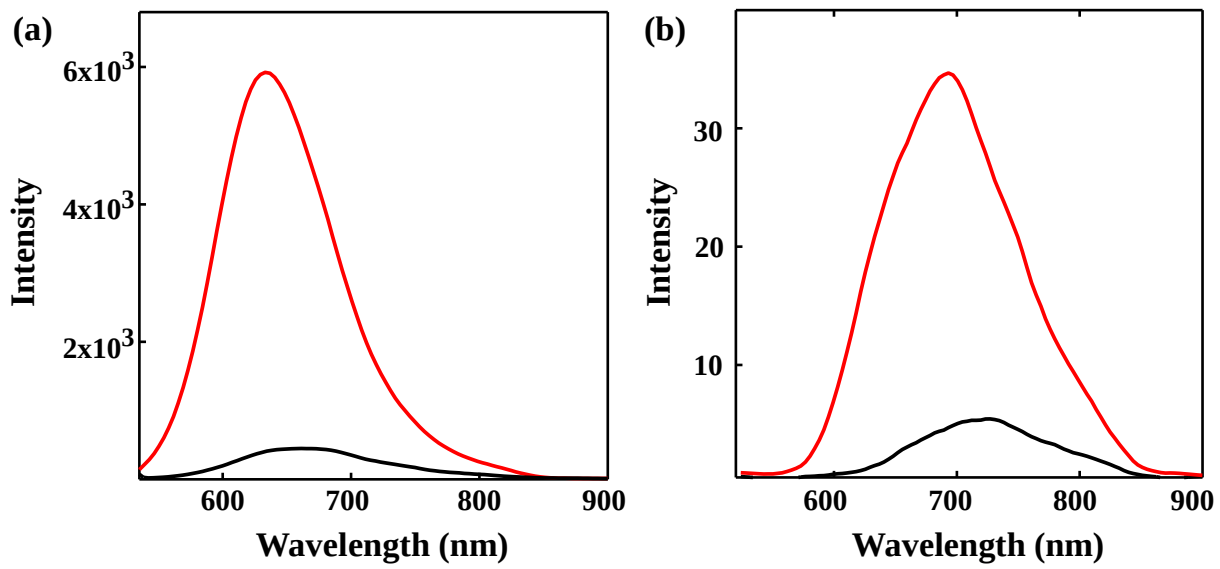

Figure S9. Luminescence spectra of (a) $Au_{22}(SG)_{18}$ (black) and TOA-A_{22} (red) and (b) $Au_{25}(SG)_{18}$ (black) and TOA-A_{25} (red). All cluster solutions have the same absorbance (0.025) at 514 nm and excited at 514 nm.

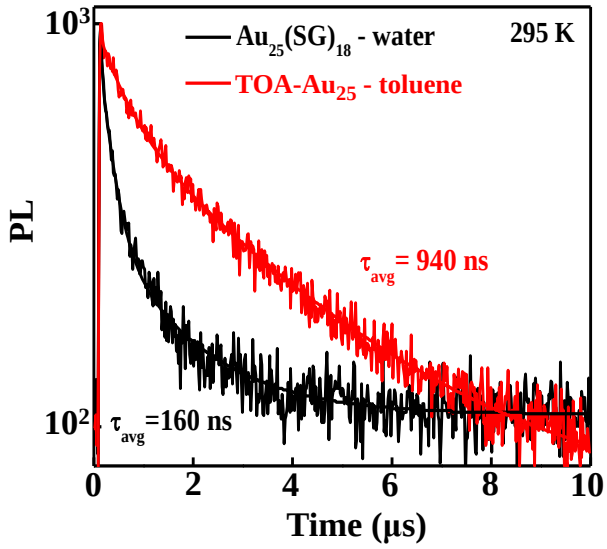

Figure S10. Luminescence decay traces of $Au_{25}(SG)_{18}$ in water and TOA-Au_{25} in toluene at 295 K. The decay traces were fitted to three exponential function and average lifetimes were determined.