Optimization of Gold Nanoparticle Photoluminescence by Alkanethiolation

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Supporting Information

Small angle X-ray scattering

The size and distribution of the thiolate-coated AuNPs were characterized by small angle X-ray scattering (SAXS). Figure S1 shows the 2D SAXS scattering patterns and the overall sizes of the thiolate-coated AuNPs of different capping agents of 3, 6, 8, 11, and 16 carbon were determined. A particulate system[1] was used to analyze the scattering data. When the particle concentration is low, the scattering of the particle in the solution (or matrix) does not mutually interact. Accordingly, the scattering intensity of individual particle, *I(q)*, could be expressed as:

$$I(q) = n_p(\rho_p - \rho_m)^2 V_p^2 P(q) S(q) \cdots\cdots (1)$$

where the wavevector $q = 4\pi\lambda^{-1}\sin\theta$ is defined by the wavelength λ and the scattering angle 2θ of X-rays; n_p is the number density of particles; ρ_p and ρ_m are the scattering density of the particle and the matrix; V_p denotes the volume of particle; $P(q)$ is the form factor; $S(q)$ is the structure factor which is ~1 in a low-concentration system and thus can be ignored. Therefore, the scattering profile of $I(q)$ is only related to the form factor $P(q)$ of the particles. As a result, *I*(*q*) can be linked to the Guinier's expression:

$$I(q) = n_p(\rho_p - \rho_m)^2 V_p^2 \exp\left(\frac{-q^2R_g^2}{3}\right)\cdots\cdots(2)$$

Where *Rg* is radius of gyration.[2,3,4] Note that in this case, ln(*I*) is linear with respect to q^2, with a slope of $-R_g^2/3$. Figure 5 (a) of the main manuscript shows the relationship between ln(*I*) and q^2 obtained from the 2D SAXS scattering patterns for 5 different thiolate-coated AuNPs. Figure 5(b) shows particle size, R_g, obtained from the slopes, increases with the carbon number from 3 to 16. Since the shape of the thiolate-coated Au NCs in the solution is close to sphere as confirmed by TEM, the particle size *d* could be deduced from $d = 2(5/3)^{1/2}Rg$.[1,5] Furthermore, the distribution of the particle size can be estimated from the change of the slopes in the low-*q* region; for instance, monodispersity corresponds to a single slope.

As a result, the calculated particle size and distribution of the thiolate-coated Au NCs as a function of carbon number of the capping agent from 3 to 16 are shown in Figure 5 (b). The particle size increases from 2.37±0.67, 3.38±0.58, 4.08±0.76, 4.26±0.71 to 5.07±0.83 nm through the carbon number form 3, 6, 8, 11, to 16.

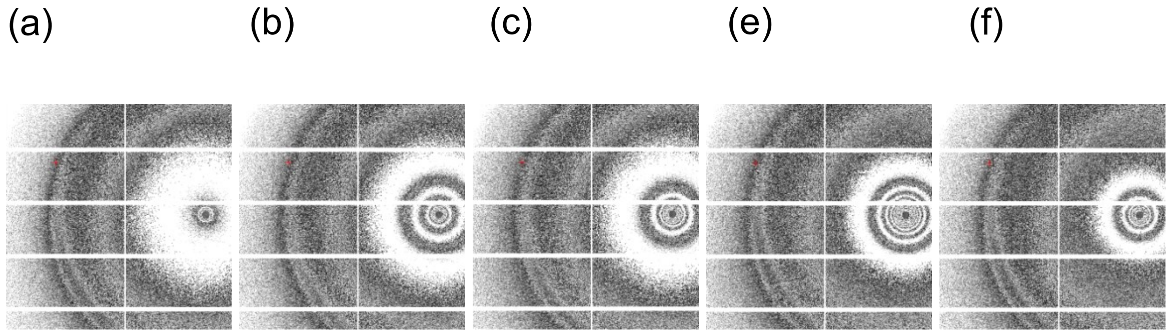

Figure S1. 2D SAXS scattering patterns for (a) 3-MPA-, (b) 6-MHA-, (c) 8-MOA-, (d) 11-

MUA-, and (f) 16-MHDA-coated Au NCs.

FTIR measurements

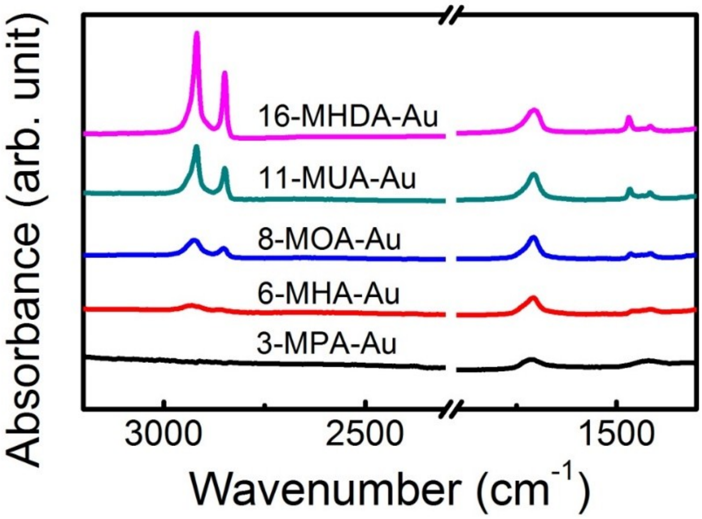

Figure S2. FTIR spectra of colloidal Au NCs synthesized in the present of different types of thiolates at R = 3.

Photoluminescence and photoluminescence excitation measurements

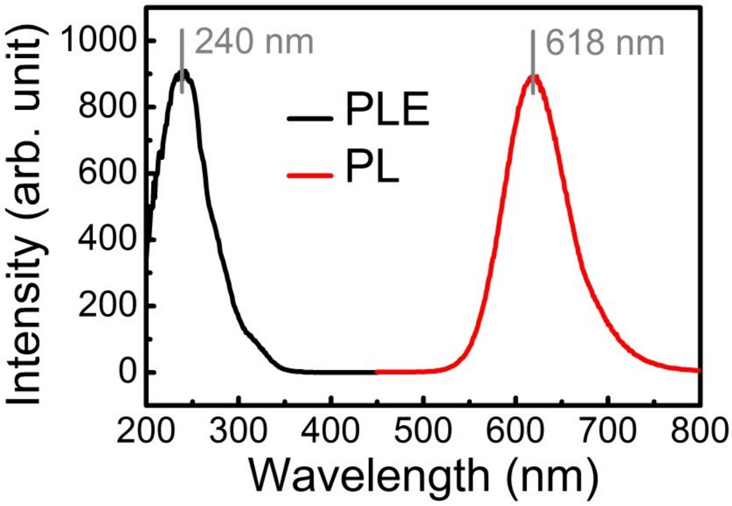

Figure S3. Photoluminescence (240 nm) and photoluminescence excitation (618 nm) spectra of the 16-MHDA-coated Au-NPs.

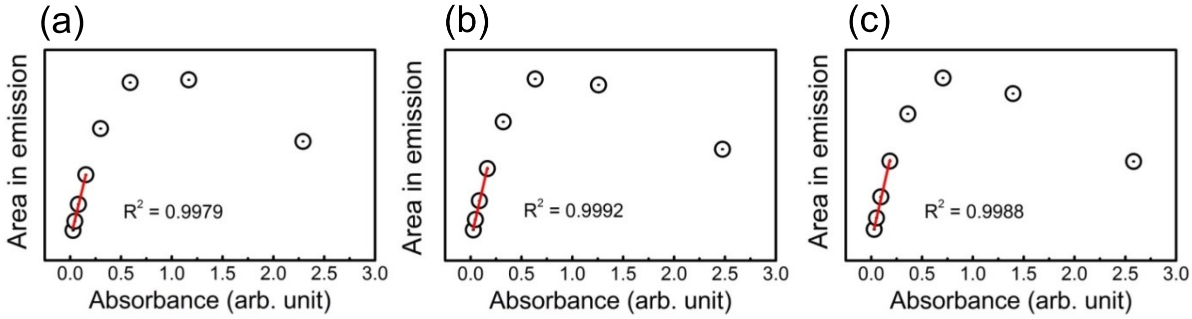

Figure S4. Linear plot of integrated area of the emission within a wavelength of 450-900 nm versus absorbance for the (a) 11-MUA-coated Au-NPs, (b) 12-MDA-coated Au-NPs and (c) 16-MHDA-coated Au-NPs. The range of linearity ($R^2 > 0.99$) is within the absorbance range 0.03-0.18.

Dynamic Light Scattering (DLS) analysis

The hydrodynamic diameters by DLS analysis are showed as below figure, the mean sizes are 1.99±0.51, 2.88±0.62, 4.40±0.91, 5.44±1.48, 6.06±1.76, 7.78±2.40 nm for the 3-MPA-, 6-MHA-, 8-MOA-, 11-MUA-, 12-MDA- and 16-MHDA-Au NPs.

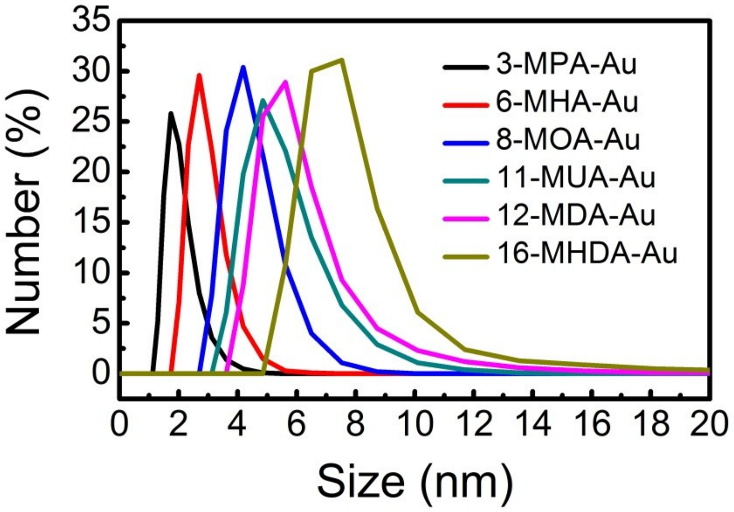

Figure S5. Mean size distribution curves for different thiolate-coated Au NCs measured by DLS.

Time-resolved photoluminescence measurement:

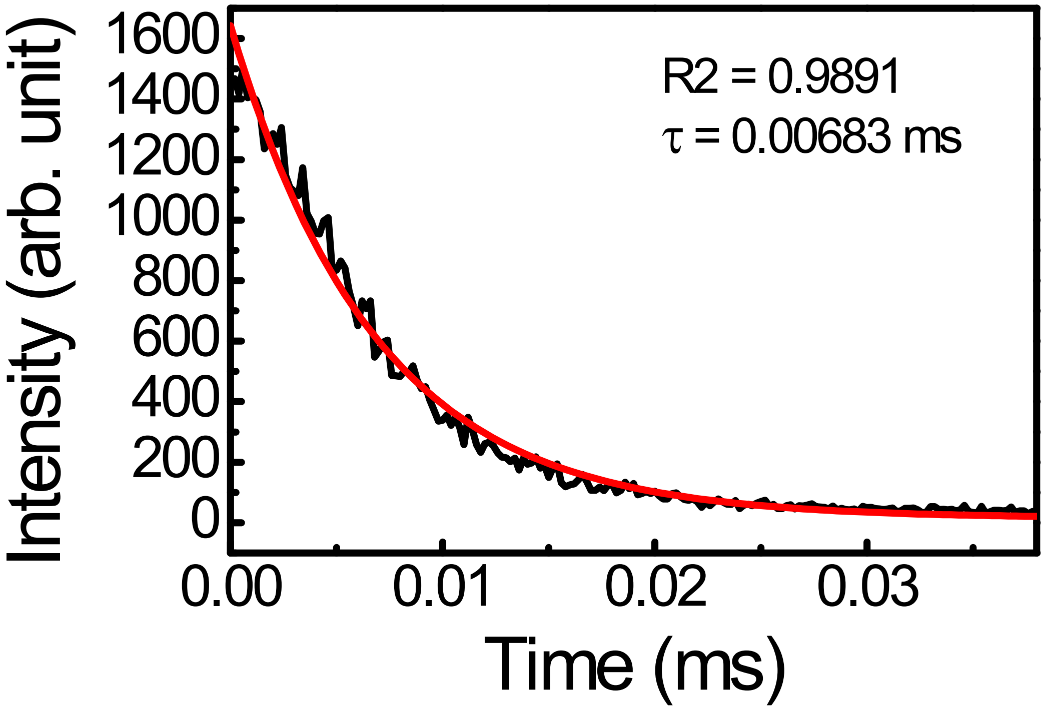

Figure S6. TRPL analysis of the MUA-Au NCs by 278 nm pulse-laser excitation.

Long shell life:

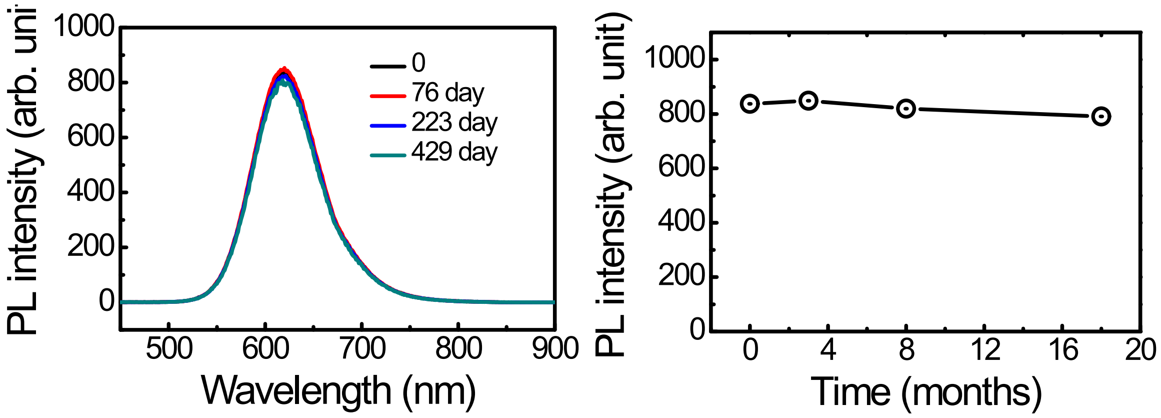

Figure S7. Photoluminescence measurement taken on 4 different time after the initial synthesis.

References

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[1] A. Guinier, G. Fournet, Small-Angle Scattering of X-rays, John Wiley & Sons, New York, 1955.

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