

Supporting Information

Modulating luminescence and assembled shape of ultrasmall Au nanoparticles towards hierarchical information encryption

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Chemicals and materials

Pluronic F127, Pluronic F108, Pluronic P123 were purchase from Sigma-Aldrich (USA); 1,3-propanedithiol (3CS₂, 98%, Meryer, China), 1, 4-butanedithiol (4CS₂, 98%, Meryer, China), 1,5-pentanedithiol (5CS₂, 96%, Macklin, China), 1,6-Hexanedithiol (6CS₂, 98%, Meryer, China), 1,8-octanedithiol (8CS₂, 97%, TCI, Japan) ethylene bis(3-mercaptopropionate) (10CS₂, >97.0 %, TCI, Japan), gold chloride hydrate (Au 48%, Meryer, China) and Tetrakis(hydroxymethyl)phosphonium chloride (THPC, 80%, J&K Scientific, China) were used as received without further purification. The cellulose membrane dialysis tubing (MWCO, 14 kDa) was purchased from Sangon Biotech (China). Ultrapure water with a resistivity of 18.2 MΩ·cm⁻¹ was produced by a Millipore Milli-Q water purifier (USA) and used for the experiments.

Optical characterization

The absorption spectrogram was obtained from a UV-2600 UV-Vis spectrophotometer (Shimadzu, Japan). The luminescence spectra ranging from 200 to 900 nm were carried out from an F4600 fluorescent spectrophotometer (Hitachi, Japan). The luminescence spectrum in the second near-infrared window region was performed from an iHR320 luminescent spectrometer (Horiba, Japan) with an 808 nm laser as the excitation light.

Structural characterization

DLS was conducted by a Nano-ZS zetasizer (Malvern, UK). The samples were put into disposable polystyrene cells, and their hydrodynamic diameters (HDs) were measured with number mode after equilibration for 120 s at 25 °C. A K-alpha instrument (Thermo Fisher Scientific, UK) performed X-ray photoelectron spectroscopy experiments using a Mono Al K α X-ray radiation

(1486.6 eV) as the excitation light source. Ar⁺ sputtering with an energy of 1000 eV acted on the samples at a rate of 0.27 nm/s for 15s to analyze the materials in-depth. The samples for XPS were prepared on the aluminum foil by dropping and air drying, and all the binding energies were calibrated using C 1s (284.8 eV) as the reference data. TEM images were acquired by a Tecnai F30 TEM (Philips-FEI, Netherlands) using an accelerating voltage of 300 kV. We counted the number of encapsulated AuNPs in each assembly from a selected area of TEM images and then constructed a statistical analysis. The particles size distributions were obtained from the TEM images, and the detailed data processing was shown as follows. A representative TEM image was selected, and particle size analyses were performed using Nano Measurer 1.2 software. After setting the scale, the size of the particles was counted in a selected area of the TEM image, and then the frequency distributions and Gaussian fitting were constructed. Particles size distribution is represented as the mean diameter \pm the standard deviation. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping were performed from a Talos F200X TEM (FEI, USA) equipped with an energy dispersive spectroscopy (EDS) system at an accelerating voltage of 200 kV. The ultrathin carbon grid contained the sample for elemental mapping entrapped by a cryo transfer tomography holder (Fischione, model 2550) with a liquid-nitrogen cooling device. Atomic force microscopy (AFM) image was carried out on a Bruker ICON Atomic force microscopy. NIR-II luminescent imaging was carried out by a NIROptics Series III 900/1700 imaging system (Suzhou, China) with an 1100 long-pass filter.

Preparation of necklace-like Au nanoassemblies (AuNAs)

Typically, 0.2 g of Pluronic F127, 27.2 μ L of 4CS₂, and 8.8 mL of water were put into a 50 mL flask and kept vigorously stirring with a magnetic stirring for 30 min to ensure the formation of a

homogeneous solution. Then, 0.8 mL of 0.1 M HAuCl₄ was added and maintained stirring to allow the color of the mixture to change from yellow to colorless. 9.8 μL of the reducer THPC was put cautiously when the pH of the above mixture was regulated to about 10 by 1 M NaOH solution and kept stirring for 24 h at room temperature. Finally, the obtained AuNAs solution was put into cellulose membrane dialysis tubing (MWCO 14 kDa) to dialyze against ultrapure water for 24 h and stored at 4 °C for further use.

For the synthesis of other Au nanoassemblies, a similar process was performed except for the amounts of some species, which were given in **Table S1**.

Table S1 The amounts of some species for the synthesis of AuNAs.

Type of AuNAs	Thiol ligand	Thiol ligand amount (μL)	Reductant	Reductant amount (μL)
3CS₂ AuNAs	3CS ₂	23.0	80% THPC	9.8
5CS₂ AuNAs	5CS ₂	31.4	80% THPC	9.8
6CS₂ AuNAs	6CS ₂	35.8	80% THPC	9.8
7CS₂ AuNAs	7CS ₂	40.6	80% THPC	9.8
8CS₂ AuNAs	8CS ₂	42.4	80% THPC	9.8
10CS₂ AuNAs	10CS ₂	44.8	80% THPC	9.8
4CS₂ AuNAs^c	4CS ₂	13.6	0.1M NaBH ₄	400
5CS₂ AuNAs^c	5CS ₂	15.7	0.1M NaBH ₄	400

Supplementary Data

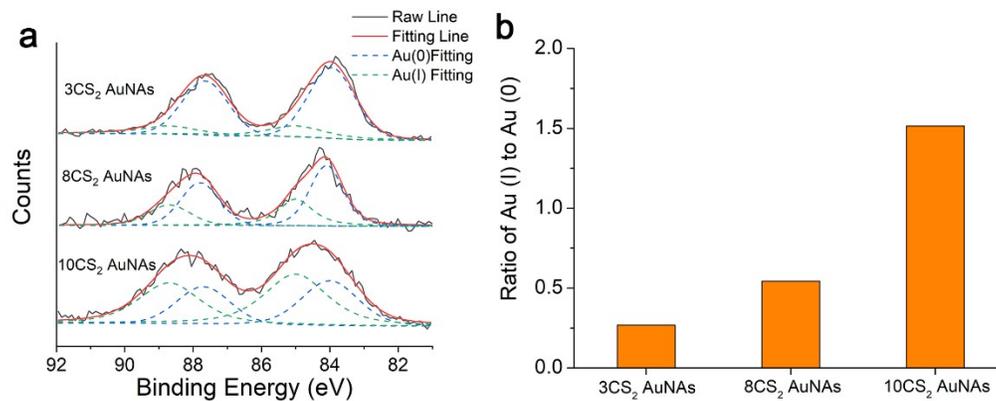


Fig. S1 (a) Au4f XPS spectra of the three types of AuNAs after Ar⁺ sputtering. (b) the ratio of Au(I) to Au(0) species of the three types of AuNAs. The blue-shifted emission could be probably attributed to the ratio of Au (I) species enhancement with increasing the carbon chain skeleton length of ligands.

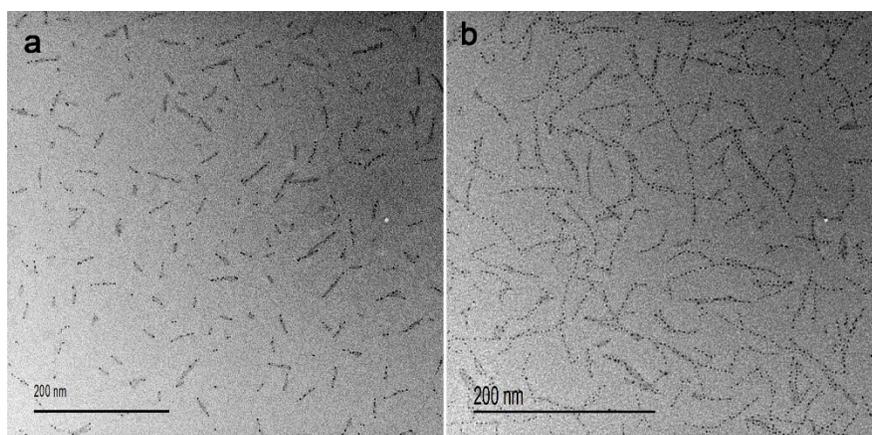


Fig. S2 TEM images of 3CS₂ AuNAs (a) and 4CS₂ AuNAs (b).

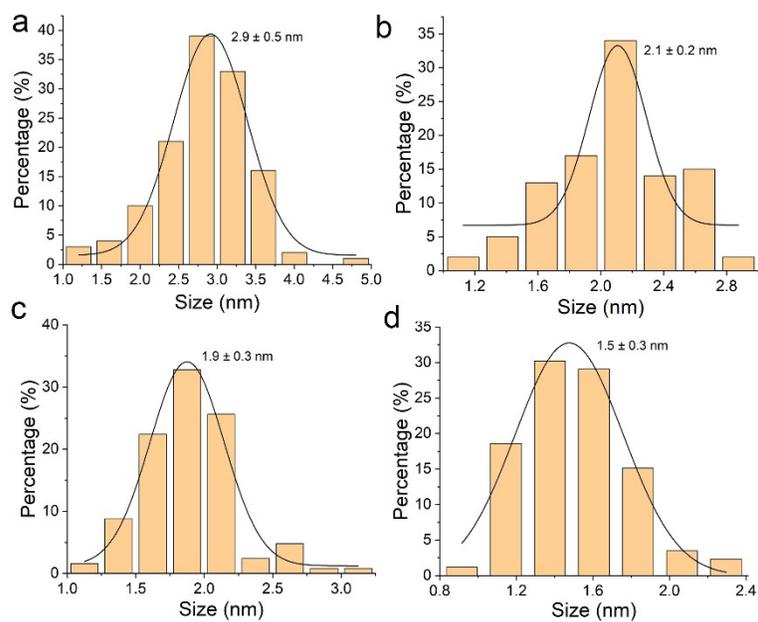


Fig. S3 The AuNPs size distribution of the 3CS₂ AuNAs (a), 4CS₂ AuNAs (b), 8CS₂ AuNAs (c) and 10CS₂ AuNAs (d) measured from TEM images.

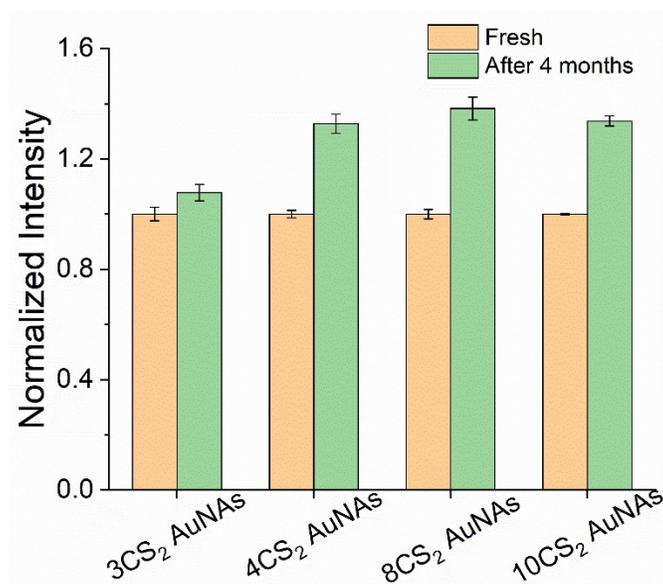


Fig. S4 The emission stability of the four types of the AuNAs after being stored in the aqueous state with an Au concentration of 700 mg·L⁻¹ at 4 °C for 4 months.

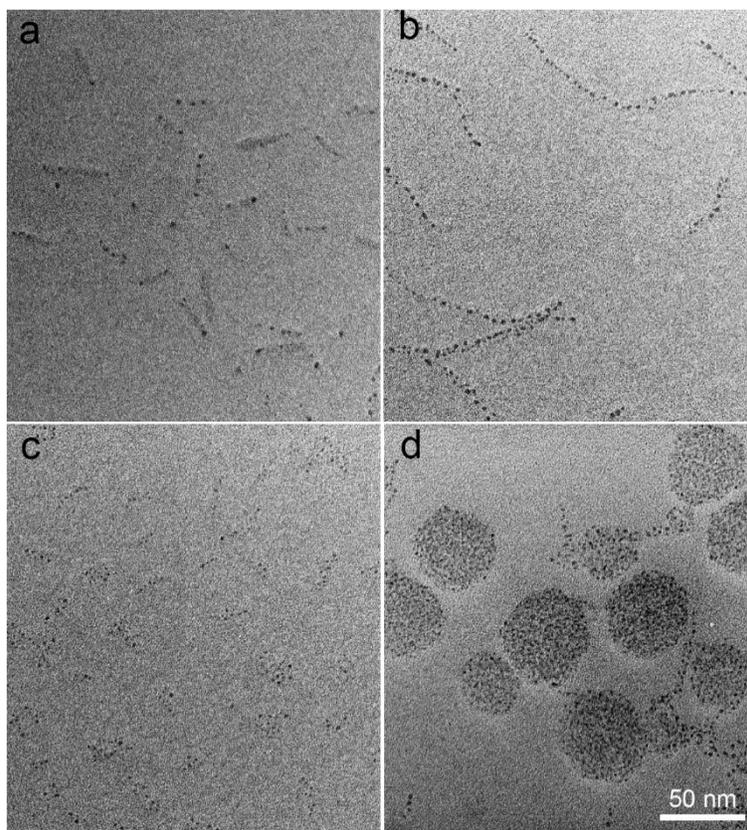


Fig. S5 The structural stability of the four types of the AuNAs after being stored in the aqueous state with an Au concentration of $700 \text{ mg}\cdot\text{L}^{-1}$ at $4 \text{ }^\circ\text{C}$ for 4 months.

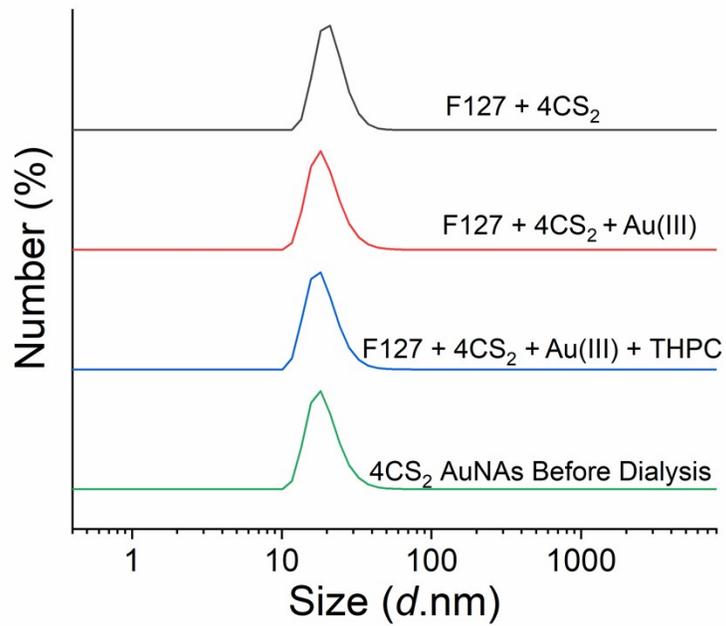


Fig. S6 The HDs of the template during the fabrication process of the 4CS₂ AuNAs.

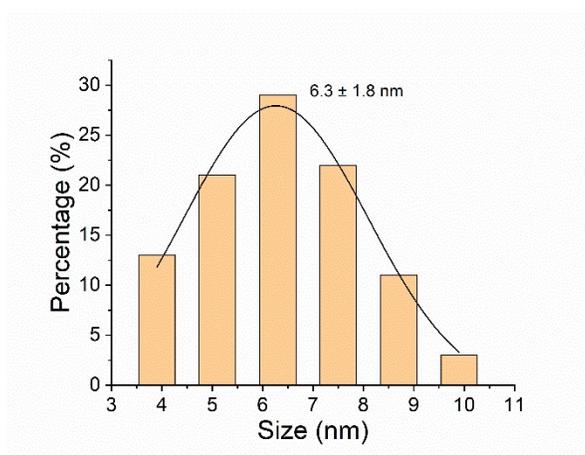


Fig. S7 The width size distribution of the 4CS₂ AuNAs from AFM image.

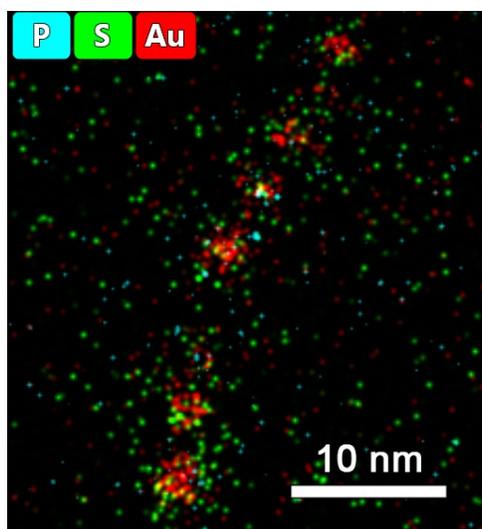


Fig. S8 Elemental mapping images for Au, S, and P element merged.

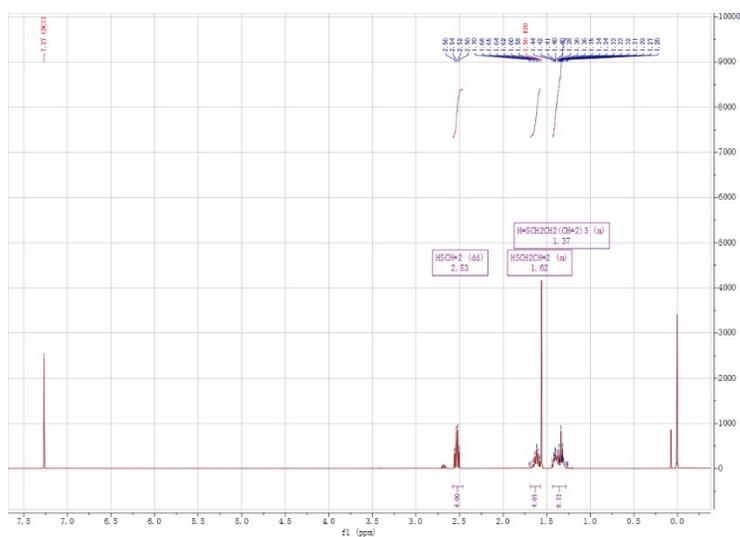


Fig. S9 ^1H -NMR spectrum of 7CS_2 ligand. ^1H NMR (400 MHz, Chloroform- d) δ 2.53 (dd, $J=7.4$ Hz, 4H, HSCH_2^*), 1.65 - 1.57 (m, 4H, $\text{HSCH}_2\text{CH}_2^*$), 1.43 - 1.28(m, 8H, $\text{H}^*\text{SCH}_2\text{CH}_2(\text{CH}_2^*)_3$). 7CS_2 ligand was prepared according to a previous report (*ACS Appl. Polym. Mater.*, 2021, **3**, 1171-1181).

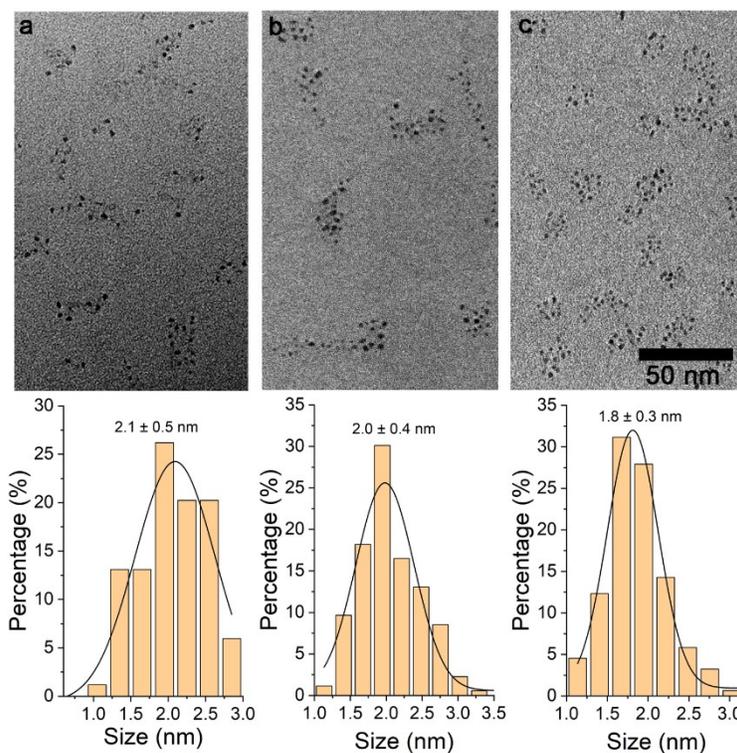


Fig. S10 TEM image of the 5CS₂ AuNAs (a), 6CS₂ AuNAs (b) and 7CS₂ AuNAs (c), and the core size distribution of the ultrasml AuNPs measured from TEM images.

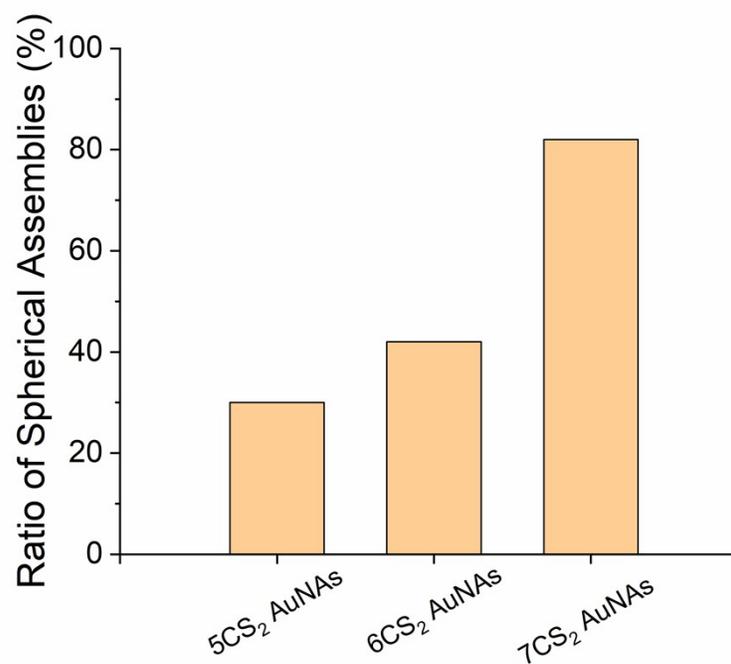


Fig. S11 The ratio of spherical assemblies from the statistics of TEM images.

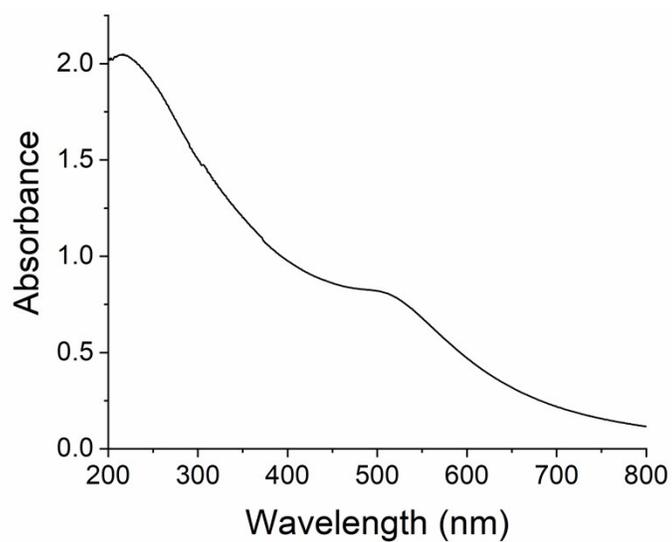


Fig. S12 UV-vis absorbance spectrum of the AuNPs prepared without bidentate thiol ligands.

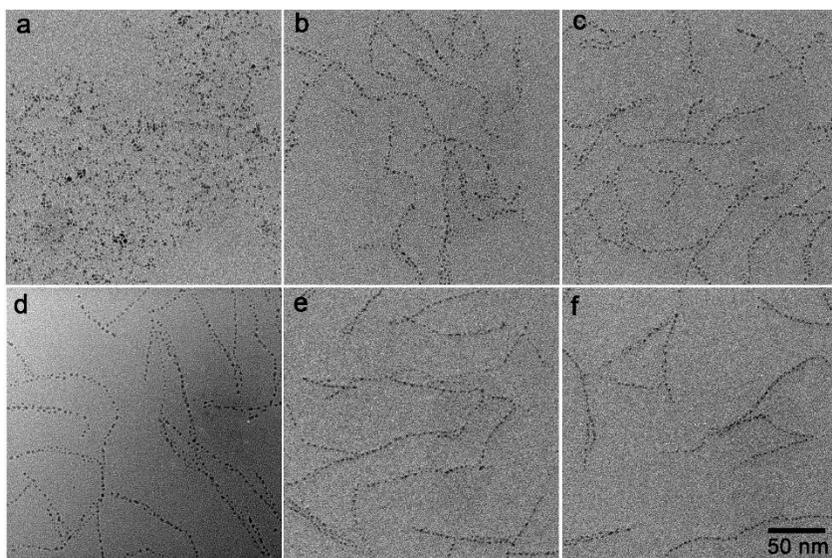


Fig. S13 The TEM images of AuNAs prepared without bidentate thiol ligands (a) and with different concentrations of 4CS₂ ligands; the ratios of Au to 4CS₂ were 1:0.7 (b), 1:1.4 (c), 1:2.8 (d), 1:5.6 (e) and 1:11.2 (f).

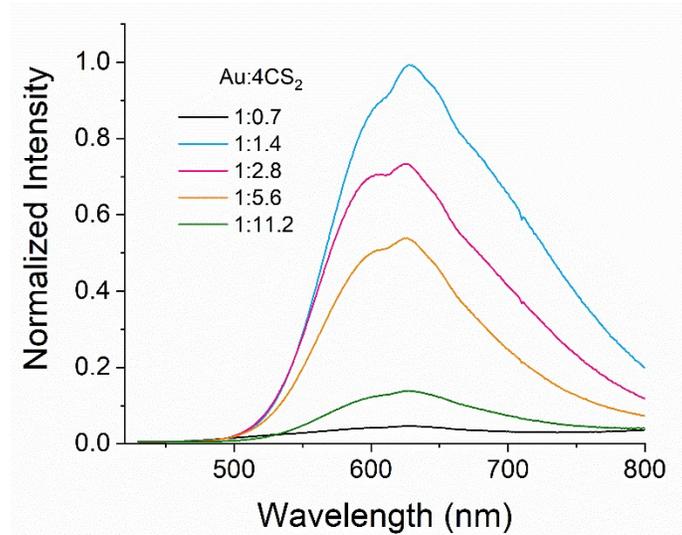


Fig.S14 The emission spectra of AuNAs prepared with different concentrations of 4CS₂ ligands.

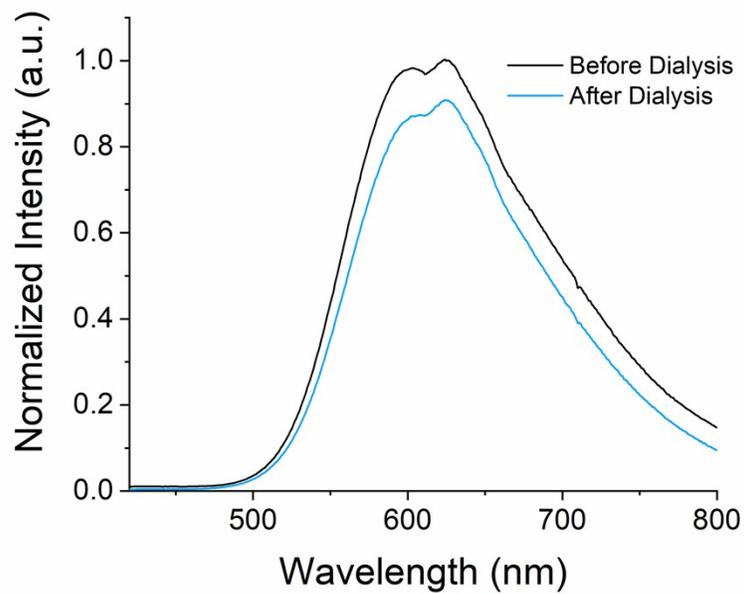


Fig. S15 The emission spectra of 4CS₂ AuNAs before and after dialysis.

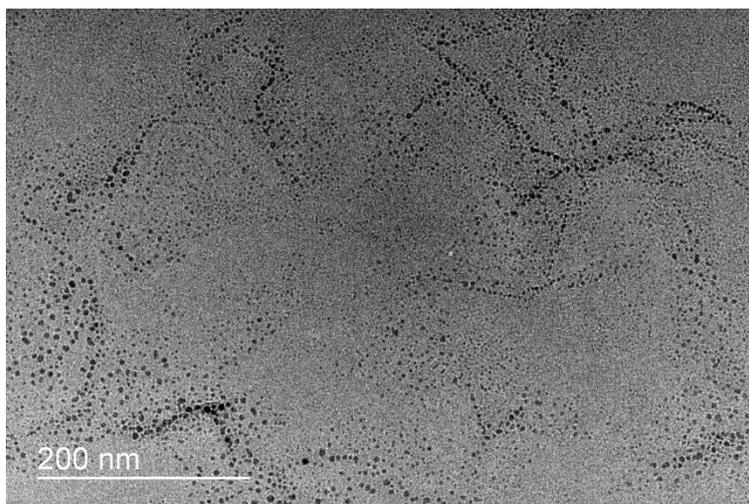


Fig. S16 TEM image of the product prepared in THF without template Pluronic F127.

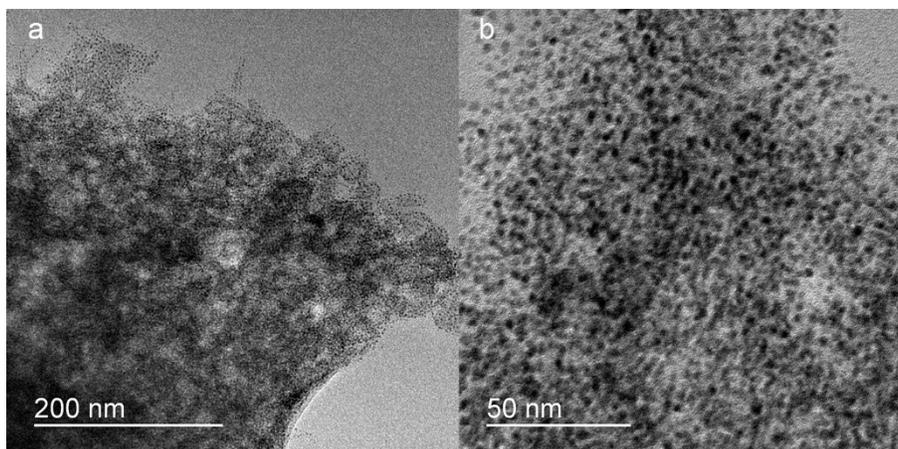


Fig. S17 TEM images of AuNAs using Pluronic P123 as template with different magnification.

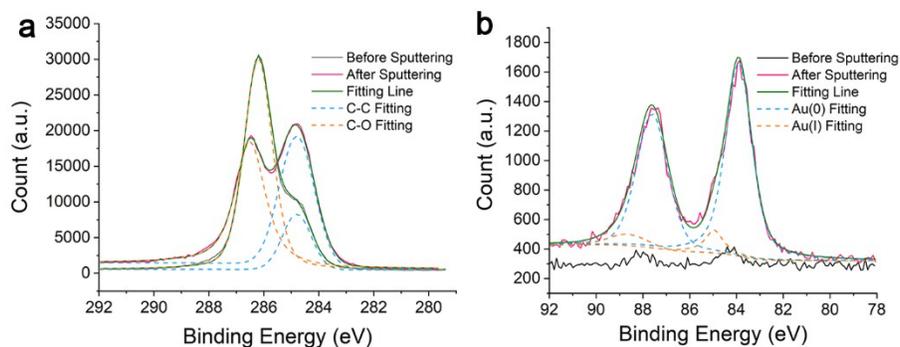


Fig. S18 C1s (a) and Au4f (b) XPS spectra of the 4CS₂ AuNAs' prepared by NaBH₄ before and after Ar⁺ sputtering.

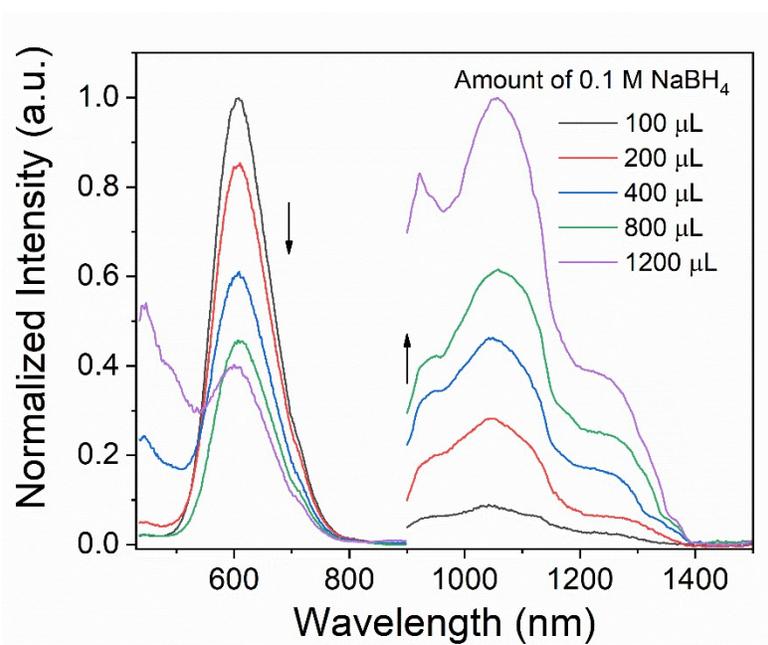


Fig. S19 The emission spectra of the 4CS₂ AuNAs using different amounts of NaBH₄. The emission spectra in the range of 430-900 nm were excited by 300 nm light, while the emission spectra in the range of 900-1500 nm were excited by an 808 nm laser.

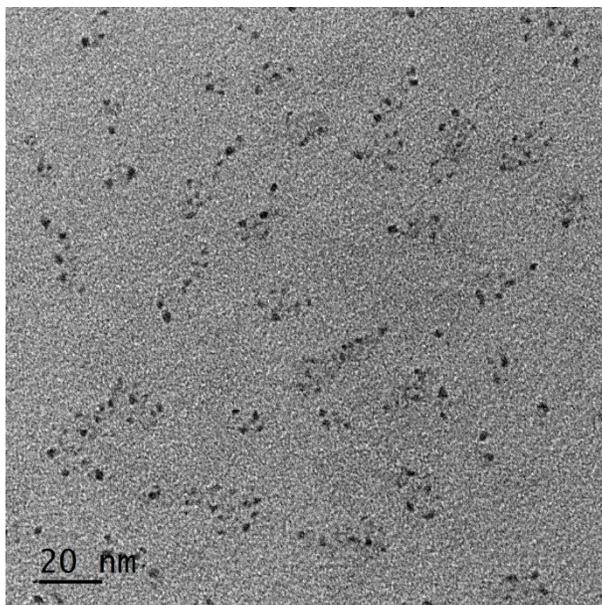


Fig. S20 TEM image of 5CS₂ AuNAs' prepared with NaBH₄.