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Supplementary Information

Ligand-regulated self-assembly of luminescent Au

nanoparticles towards diverse controllable superstructures

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Experimental Section

Chemicals and materials

Pluronic F127 (Sigma-Aldrich, USA), Ethyl 3-mercaptopropinonate (S₁, >98%, TCI, Japan), Pentaerythritol tetra(3-mercaptopropionate) (S₄, >90%, TCI, Japan), Gold chloride hydrate (Au 48%, Meryer, China) and Tetrakis(hydroxymethyl)phosphonium chloride (THPC, 80%, J&K Scientific, China) were used as received. All other reagents were purchased from Aladdin (China) and used as received without further purification. The cellulose membrane dialysis tubing (MWCO, 14 kDa) were purchased from Sangon Biotech (China). Ultrapure water with a resistivity of 18.2 M Ω ·cm⁻¹ was obtained from Millipore purification system (USA) for the experiments' use.

Optical characterization and dynamic light scattering (DLS)

The absorption spectra were collected with a UV-2600 UV-Vis spectrophotometer (Shimadzu, Japan). The luminescence spectra were performed on an F-4600 fluorescent spectrophotometer (Hitachi, Japan). Lifetimes were performed from an LP-920 laser flash photolysis spectrometer (Edinburgh, UK) equipped with an ICCD detector. The quantum yields were recorded with an absolute PL quantum yield spectrometer C11347 (Hamamatsu Photonics, Japan). DLS was obtained from a Nano-ZS zetasizer (Malvern, UK). The samples held by disposable polystyrene cells were equilibrated for 120 s at the specific temperature before the measurement.

X-ray photoelectron spectroscopy (XPS)

The samples dripped over the aluminum foil and then left to dry naturally. XPS measurements were collected with an ESCALAB 250Xi instrument (Thermo Scientific, UK) equipped with an excitation source of Al K α X-ray radiation (1486.6 eV). Ar⁺ sputtering was employed for an in-depth analysis of the species. C 1s with 284.8 eV was used as reference energy for calibration of all the binding energies.

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and scanning transmission electron microscopy in SEM (STEM-in-SEM).

The sample was prepared by $15 \times$ dilution of the original sample, and 4 μ L of the samples dripped over ultrathin carbon grids, and the excess solution was gently wiped with a filter paper after 2 min, left to dry naturally for further use. TEM images were carried out with a Tecnai F30 TEM (Philips-FEI, Netherlands) using an accelerating voltage of 300 kV. SEM and STEM-in-SEM images were obtained with SU8220 SEM (Hitachi, Japan) using an accelerating voltage of 10 kV and 5 kV, respectively. High angle annular dark-field STEM (HAADF-STEM) image and elemental mapping were conducted on a Talos F200X TEM (FEI, USA) with energy dispersive spectroscopy (EDS) system at an accelerating voltage of 200 kV. The samples for the HAADF-STEM image and elemental mapping were placed on a cryo transfer tomography holder (Fischione, model 2550) with a liquid-nitrogen cooling system. The cryo holder could maintain the samples at a temperature of less than -160 °C during data collection. At that temperature, the hydrocarbon contamination accumulation was minimized due to the remarkable reduction of the thermal diffusion effect. Also, the fragile samples thus could be protected under the electron beam, since the thermal effect of electron-probe current was dramatically decreased. To acquire high-quality images and accurate EDS, the data for every sample were collected for 15 min, and element EDS spectra of Au, S and P atoms were acquired simultaneously in the same area with an automatic drift correction. Data analysis was performed using Velox. The elemental mapping for Au atom was computed using extracted net intensity of the L α line after background subtraction, while the elemental mapping for S and P atoms were calculated using the extracted net intensity of their respective Ka lines after background subtraction.

Synthesis of a series of gold nanoassemblies (AuNAs)

In a typical synthesis of S_4 AuNAs, 0.2 g of pluronic F127, 54.8 mg of S_4 , 8.8 mL of ultrapure water were added in sequence into 50 mL flask (Xinweier, Beijing), after the formation of a homogeneous solution under vigorous stirring using a magnetic stirrer (IKA RCT Basic, Germany), 0.8 mL of 0.1 M HAuCl₄ was added dropwise into the above solution followed by the adjustment pH to 10.0 with 1 M NaOH. Then, 9.8 μ L of THPC was added slowly into the above mixture, and the mixture solution was allowed to proceed for 24 h under stirring at room temperature before incubation at 4 °C for another 6 h. The S₄ stabilized AuNAs (S₄ AuNAs) were obtained after dialysis against ultrapure water for 24 h through cellulose membrane dialysis tubing (MWCO 14 kDa) and stored at 4 °C for further use.

For fabricating the AuNAs stabilized by other thiol ligands, a similar process was performed except the amount of thiol ligands. For example, 58 μ L of S₁.



Supplementary Data

Fig. S1 The equation for the oxidation reaction of THPC to produce tri(hydroxymethyl) phosphine oxide (THPO). THPC could react with NaOH to give tris(hydroxymethyl)phosphine and formaldehyde. Tris(hydroxymethyl)phosphine was unstable under base condition, and then produced THPO and H_2 .¹



Fig. S2 Time-resolved decay of the S₄ AuNAs and S₁ AuNAs. The decay of the S₄ AuNAs can be fitted with a sum of two components at 0.414 μ s (20.9%) and 1.802 μ s (79.1%), and the decay of the S₁ AuNAs can be fitted with a sum of two components at 0.036 μ s (49.3%) and 0.337 μ s (50.7%).



Fig. S3 P 2p (a) and S 2p (b) XPS spectra of the S_1 AuNAs before and after Ar^+ sputtering.



Fig. S4 C1s (a), Au4f (b), S2p (c) and P2p (d) XPS spectra of the S₄ AuNAs before and after Ar⁺ sputtering.



Fig. S5 TEM images of the S_4 AuNAs (a) and the S_1 AuNAs (b), and size distribution of AuNP core, inset showed the high resolution TEM image of the AuNAs.



Fig. S6 STEM-in-SEM images of the S_4 AuNAs (a) and the S_1 AuNAs (b).



Fig. S7 HDs of the S₄ AuNAs and the S₁ AuNAs at different pH (a) and temperatures (b). (c) TEM image of the S₁ AuNAs after incubation at 50 °C for 30 min. Both AuNAs exhibited outstandingly stable against pH or temperature change, as the HDs of the S₄ AuNAs and the S₁ AuNAs could still keep about 36 nm and 65 nm without obvious change even when pH altered in the range of 4-10 or temperature changed from 4 to 50 °C. Even at 50 °C, the S₁ AuNAs still remained the noticeable fiber-like nanostructures.



Fig. S8 (a) Elemental mapping images for Au, S, and P merged. (b) Elemental profiles of Au, S, and P acquired along the green line indicated in (a).



Fig. S9 (a) Elemental mapping images for Au, S, and P merged. (b) Elemental profiles of Au, S, and P acquired along the green line indicated in (a).



Fig. S10 TEM (a, b) and STEM-in SEM (c) images of the product prepared using S_4 but without pluronic F127.



Fig. S11 TEM (a) and high-resolution TEM (b) images of the product prepared with a similar process of the S_4 AuNAs but the reaction condition changed to 4 °C before adjusting mixture pH. The thermo-sensitivity of pluronic F127 afforded controllable location of the ultrasmall AuNP. The cross-linking interaction between Au (I) and multidentate thiol ligand S_4 occurred and enhanced the micelles stability. Even if the hydrophobic region is turned hydrophilic at 4 °C,² F127 could still remained micelles. The micelles resulted in the homogeneous distribution of the ultrasmall AuNP all over the template interior.



Fig. S12 SEM image of the product prepared by a similar process of the S_1 AuNAs without using THPC.



Fig. S13 (a) TEM image of S_1 AuNAs just handled by dialysis without 4 °C incubation. (b) HDs of S_1 AuNAs at different dilution times.



Fig. S14 TEM images of the S_1 AuNAs after incubation for different times under 4 °C. The samples for TEM images did not undergo the dialysis process.



Fig. S15 TEM image of the product with ratios of S_1 to Au atom of 16.8.



Fig. S16 S2p XPS spectra of the S_4 AuNAs at different ratios of S_4 to Au atom before Ar⁺ sputtering. With increasing the ratio of S_4 to Au atom, the signal for thiol ligand gradually enhanced, suggesting excess S_4 spilled over and generated hydrophobic patches on the template surface during *in situ* fabrication.



Fig. S17 (a) Au4f XPS spectra and (b) Au(I) species of the S_4 AuNAs at different ratios of S_4 to Au atom after Ar⁺ sputtering.



Fig. S18 TEM images of MH-stabilized AuNAs and S₂-stabilized AuNAs.

References

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