

Electronic supplementary information for

Blue Light Emitting Gold Nanoparticles Functionalized with Non-thiolate Thermosensitive Polymer Ligand: Optical Properties, Assemblies and Application

1. Experimental section

1.1 Materials

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99%) was obtained from Sinopharm Chemical Reagent Co. Ltd. L-ascorbic acid (*L*-Aa) was purchased from Beijing chemical works. Thiazolyl blue tetrazolium bromide (MTT) was purchased from Sigma-Aldrich. N-isopropylacrylamide (NIPAM, Aldrich) was recrystallized in hexane. Other chemicals were of analytical grade without purification. Solutions of metal ions were all prepared from their chloride salts.

1.2 Synthesis of copolymer ligand of p(NIPAM-co-MQ)

5-(2-Methacryloyloxyethyl)-8-quinolinol (MQ) was synthesized according to a previous procedure. The novel copolymer ligand (CPL) of p(NIPAM-co-MQ) was prepared by conventional free radical copolymerization of NIPAM and MQ monomers as described in our previous work.

1.3 Synthesis of CPL-stabilized gold nanoparticles (Au NPs-a) by L-ascorbic acid

All glassware used in the experiment was cleaned in a bath of freshly prepared aqua regia

(HCl : HNO₃, 3 : 1 by volume) and rinsed thoroughly in water prior to use. In a typical experiment, 0.5 mg of HAuCl₄ (0.25 mmol) was added into 5 mL of CPL aqueous solution with different molar concentrations under vigorous stirring (the samples from Au a-1 to Au a-7 represent the CPL-capped Au NPs with the molar feed ratios of [HAuCl₄]/[CPL]=1:1, 1:5, 1:10, 1:20, 1:30, 1:40 and 1:50). After 30 min, a certain concentration of *L*-Aa solution was added, and the mixture was incubated at room temperature. The solution was then dialyzed in double distilled water for 48 h and the final solution was stored at 4 °C until use.

1.4 Synthesis of CPL-stabilized gold nanoparticles (Au NPs-b) at basic pH conditions

Au NPs-b was synthesized using a modified procedure described in the preparation of *Au NPs-a*. In a typical synthesis, different pH values of hartshorn from 7 to 10, instead of *L*-Aa, added into the mixture of HAuCl₄ and CPL under vigorous stirring. The solution was then dialyzed in double distilled water for 48 h. The final obtained Au NPs were stored at 4 °C when not in use.

1.5 Synthesis of CPL-stabilized gold nanoparticles (Au NPs-e) by etching Au NPs

The Au NPs were prepared according to the Turkevich method¹ in which the HAuCl₄ is reduced to Au NPs using sodium citrate. Au NPs-e is obtained from a ligand exchange reaction and ligand-induced etching process. Simply, the CPL was added into the as prepared Au NPs solution and stirred at room temperature for more than one week.

1.6 In vitro cytotoxicity in HeLa cells and cell imaging

The MTT toxicity test of Au NPs in HeLa cells was operated as described by Li et al.² HeLa cells were seeded in a 96-well plate in cell medium overnight and, subsequently,

incubated with different concentrations of Au NPs-b (0, 15, 30, 60, 125 and 250 $\mu\text{g ml}^{-1}$) in cell medium for 2 h at 37 °C and 5% CO_2 . Four replicate samples were prepared for each concentration. After removing Au NP-containing medium and washing twice with sterile PBS, cells were further incubated in cell medium for 24 h at 37 °C and 5% CO_2 . Afterwards, 10 μL MTT were added to each well. After incubation for 4 h at 37 °C and 5% CO_2 , 150 μL DMSO was added to each well and mixed thoroughly before finally measuring the absorbance of the solution at 490 nm. Fluorescence images of HeLa cells incubated with Au NPs-b were collected on a Leica TCS 4Pi scanning confocal laser microscope (Leica Microsystems).

1.7 Characterization

$^1\text{H-NMR}$ spectra were obtained from an AVANCE Bruker spectrometer at basic frequencies of 500 MHz for ^1H in CDCl_3 solution. UV-vis absorption spectra were recorded on a SHIMADZU UV-2550 UV-visible spectrophotometer in the range 200—800 nm. The photoluminescence properties were measured on FLSP920 Edinburgh Fluorescence Spectrometer. Luminescence lifetime were measured with a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using a 355 nm laser radiation (pulse width = 4 ns) as the excitation source (Continuum Sunlite OPO). The molecular weights of polymers were estimated at a flow rate of 1.0 mL min^{-1} at 25 °C by gel permeation chromatography (GPC) on a Waters instrument (Waters Corporation, USA), using CHCl_3 as eluent, and the molecular weights were determined vs polystyrene standards. Transmission electron microscopy (TEM) was carried out on a JEM-2100F electron microscope. X-ray photoelectron spectroscopy (XPS, PHI5000 ESCA, Perkin Elmer, USA) equipped with Al $\text{K}\alpha$ source (1486.6 eV photons) was used to characterize the Au NPs.

References

- 1 B. V. Enüstün, J. Turkevich, *J. Am. Chem. Soc.* **1963**, *85*, 3317.

2 S. Li, L. Yang, F. Stockmar, R. Popescu, V. Trouillet, M. Bruns, D. Gerthsenb, G. U. Nienhaus,

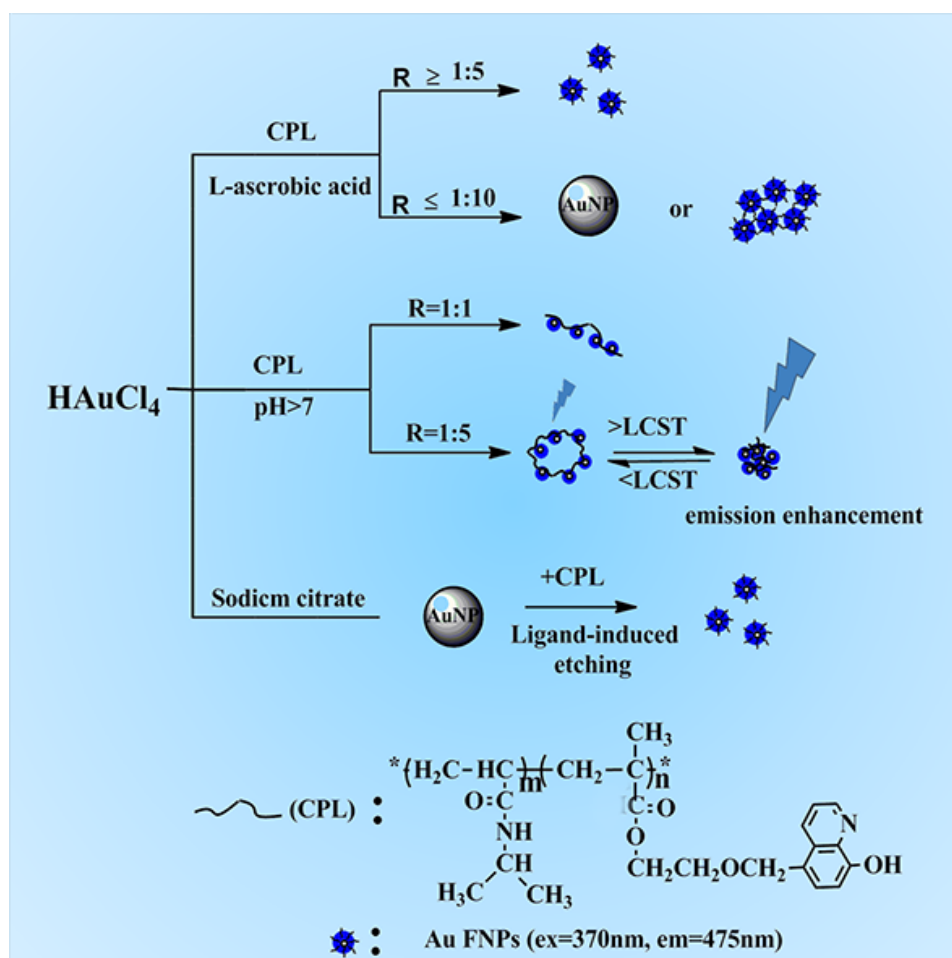
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2. Supporting Figures



Scheme S1. Schematic illustration of the synthetic route of Au NPs and their integration features with blue light emission, thermoresponse and self-assembly. R refers the Au/CPL mole ratios.

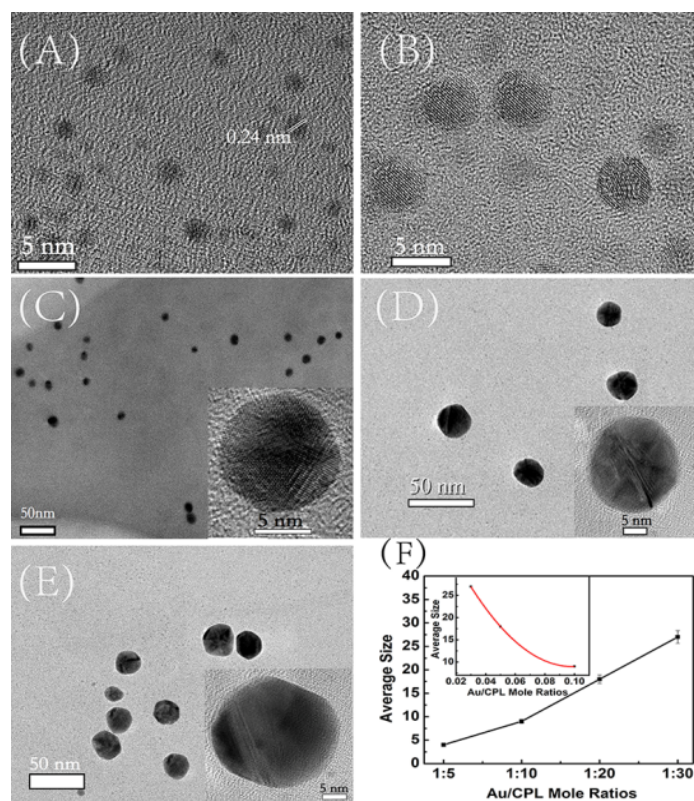


Fig. S1. TEM images of Au NPs-a with different Au/CPL ratios: (A) 1:1, (B) 1:5, (C) 1:10, (D) 1:20, (E) 1:30 and (F) Size dependence of Au NPs with decreasing Au/CPL ratio. Insert: binomial relationship between NPs size and Au/CPL ratio. the size dependence of Au NPs-a on Au/CPL ratios can be fitted with the following binomial relationship: $\varnothing = 3857R^2 - 759R + 46$. Where \varnothing is the average size of Au NPs and R ($0.03 < R \leq 0.5$) is the Au/CPL mole ratios. Thus, the growth of Au NPs can be easily controlled from near 2 nm to 30 nm by adjusting the Au/CPL ratios and the fluorescent gold nanoparticles (Au FNPs) can be obtained when the Au/CPL ratio is 1:1.

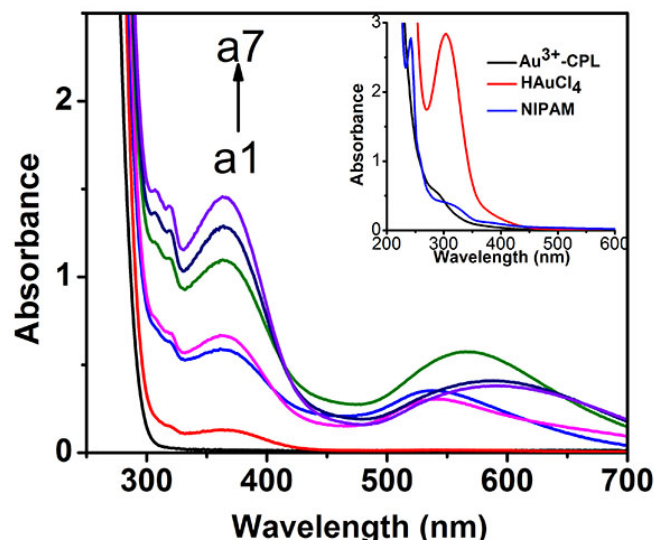


Fig. S2. UV-vis absorption spectra of Au NPs-a.

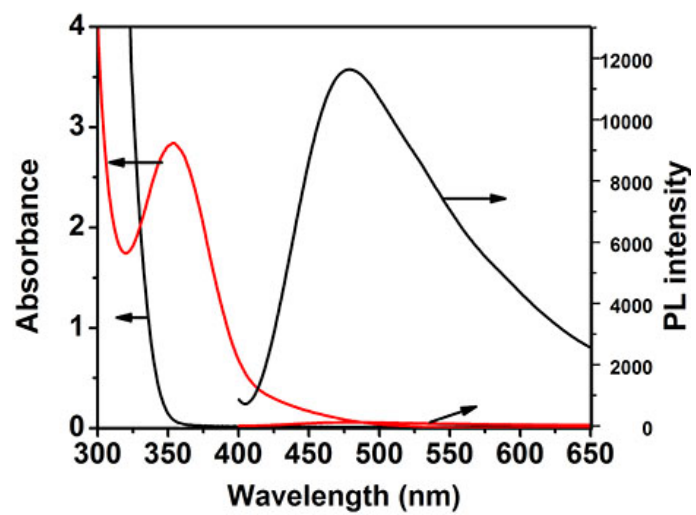


Fig. S3. UV-vis absorption and PL spectra of Au NPs before and after treating with MPA (0.5 M).

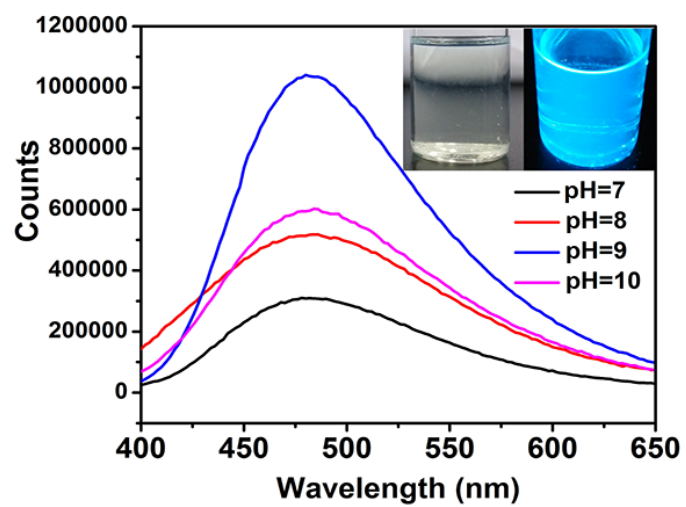


Fig. S4. PL spectra of Au NPs-b with different pH values. Insert: digital images of Au NPs-b under daylight and UV lamp at pH=9.

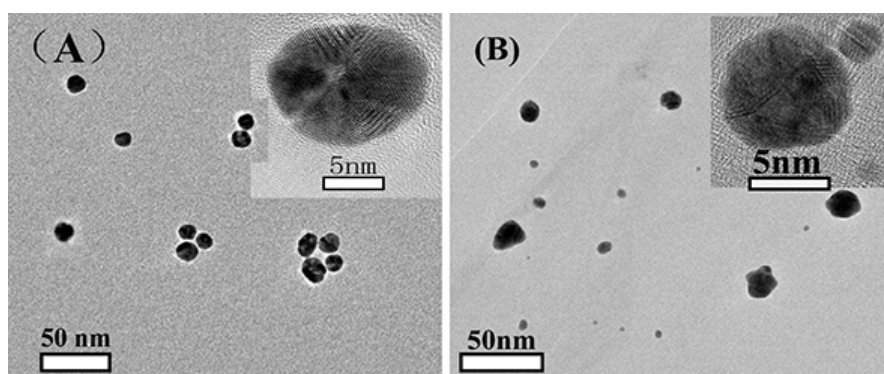


Fig. S5. TEM images of Au NPs (A) before and (B) after ligand exchange with CPL. The small Au NPs and the larger size of particles can be seen in the TEM image, indicating that they have reacted incompletely.

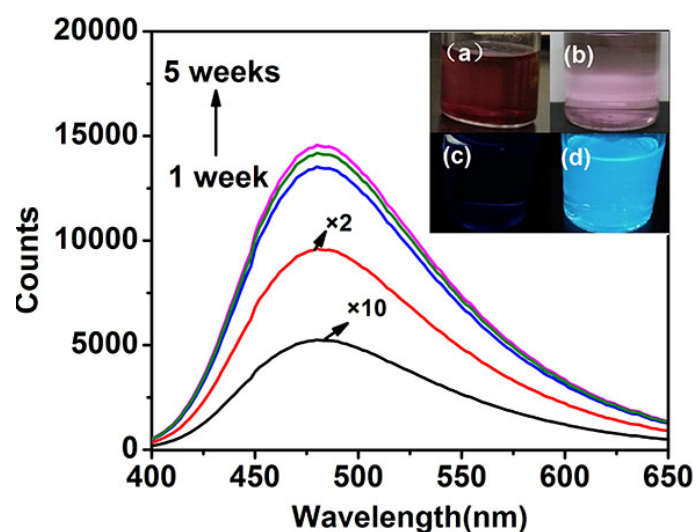


Fig. S6. PL spectra of Au NPs-e after etching citrate capped 13 nm Au NPs for different weeks. Inset shows digital images collected under white light (a and b) and UV irradiation (c and d) for Au NPs before (a and c) and after (b and d) etching for 5 weeks. The black line and red line are the PL spectra expanded ten and two times, respectively. We assume that the generation of fluorescent Au NPs-e is responsible for the size reduction of the nanocrystals after ligand exchange and ligand-induced etching. For the ligand-induced etching, the surface-Au atoms of Au NPs are removed leading to the formation of Au(I)-quinolinol complexes and these complexes can then undergo strong Au(I)-Au(I) interactions to form Au FNPs. This hypothesis is in agreement with the broad size distribution of Au NPs-e from the TEM images after etching (see **Fig. S5**).