

Electronic Supplementary Information

**Synthesis and Electrochemiluminescence of
Bis(2,2'-bipyridine)(5-amino-1,10-phenanthroline)
Ruthenium(II) -Functionalized Gold Nanoparticles**

Yuqi Yu,^a Ming Zhou,^b Hua Cui*^a

^aCAS Key Laboratory of Soft Matter Chemistry, Department of Chemistry,
University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.

^bCenter for in vitro Diagnostic Technologies, Suzhou Institute of Nano-Tech and
Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu 215123, P. R. China.

Experimental Section

Chemicals and solutions: A H₂AuCl₄ stock solution (H₂AuCl₄, 2% w/w) was prepared by dissolving 1.0 g of H₂AuCl₄·4H₂O (Shanghai Reagent, China) in 412 mL of purified water and stored at 4 °C. Tripropylamine (TPrA) was purchased from Sigma-Aldrich (USA). NaBH₄ was purchased from Shanghai Reagent, China. Bis(2,2'-bipyridine)(5-amino-1,10-phenanthroline) ruthenium(II) bis(hexafluorophosphate) [denoted as Ru(bpy)₂(NH₂-phen)²⁺] was obtained from Suna Tech Inc. (Suzhou, China). A 0.1 mM stock solution of Ru(bpy)₂(NH₂-phen)²⁺ was prepared by dissolving Ru(bpy)₂(NH₂-phen)²⁺ in 0.1 M NaOH solution and was kept at 4 °C. A 0.05 mM stock solution of tripropylamine was prepared in 0.05 M

phosphate buffer (pH 7.5). All other reagents were of analytical grade. Ultrapure water was prepared by a Milli-Q system (Millipore, France) and used throughout.

Synthesis and characterization of AuNPs: All glassware used in the following procedures was cleaned in a bath of freshly prepared HNO₃-HCl (3:1, v/v), rinsed thoroughly in ultrapure water, and dried prior to use. Gold colloids were prepared via the reduction of HAuCl₄ with NaBH₄ in the presence of Ru(bpy)₂(NH₂-phen)²⁺. A 1 mL of HAuCl₄ stock solution and 0.1 mL of Ru(bpy)₂(NH₂-phen)²⁺ stock solution was mixed with 20 mL ultrapure water, then the pH of the mixture was adjusted to 12 by NaOH. While stirring intensely, the resulting solution turned to red or wine-red with the addition of an aqueous solution of NaBH₄ (0.075 % w/w, 0.020 mol L⁻¹). NaBH₄ volumes of 0.1, 0.25, 0.5 and 1.0 mL were selected for synthesis. As-prepared colloidal gold dispersions were subsequently characterized by HRTEM (Jeol Ltd., JEOL-2010, Japan) and UV-visible absorption spectra (Agilent 8453 UV-visible spectrophotometer, USA). The histograms were obtained by measuring the diameters of nanoparticles (n > 100) in TEM photomicrographs. Colloidal gold prepared with 0.25 mL of NaBH₄ after dialysis were chosen for XPS characterization and for further use. The dialysis procedure was used to remove the unreacted reagents and the resulted products from the as-prepared AuNPs solutions with 3500 molecular weight cutoff dialysis membrane by 3 days. Then the AuNPs was centrifuged at 15000 rpm for 1 h (Universal 320, Hettich, Germany), and the sediment was resuspended in ethanol by ultrasonic dispersion process to removing inorganic or organic impurities completely. Finally the purified AuNPs were dried under vacuum at 60 °C for XPS

detection. XPS was performed on an ESCALABMK II electron spectrograph (VG Scientific, UK) with Al K α radiation as the X-ray source. The XPS data were fitted by XPSPeak and further plotted by OriginPro 7.0. Element analysis of the isolated dialyzed material was carried out by X-ray photoelectron spectroscopy. It was found that the ratio of atoms of Ru and Au was 1:64.

ECL and PL measurements of the as-prepared AuNPs: ECL and electrochemical (EC) measurements were performed by using a homemade ECL/EC system, including a model CHI760D electrochemical working station (Chenhua Inc., China), a H-type electrochemical cell (self-designed), a model CR-105 photomultiplier tube (PMT) (Beijing, China), a model RFL-1 luminometer (Xi'an, China), and a computer as described previously.¹⁻² A gold electrode served as the working electrode in the present work. When a potential was scanned on the gold electrode from 0.0 to 1.6 V, an ECL signal was generated and recorded by the RFL-1 luminometer. The curves of ECL intensity versus applied potential and the cyclic voltammograms were recorded simultaneously. As-prepared AuNPs solution was all used after thorough dialysis for 24 h. A bare gold electrode was used as working electrode to measure the ECL intensity of the as-prepared gold colloids by cyclic voltammetry in 0.05 M phosphate buffer containing 0.05 M TPrA in aqueous solution. PL measurements were performed by using a F-7000 fluorometer (Hitachi, Japan) with a 150 W Xe lamp as the light source. The excitation wavelength was 455 nm. The concentration of Ru(bpy)₂(NH₂-phen)²⁺ was 0.5 μ M while the as-prepared AuNPs remained the concentration of synthesis.

References

1. H. Cui, Y. Xu and Z. F. Zhang, *Anal. Chem.*, 2004, **76**, 4002-4010.
2. H. Cui, G. Z. Zou and X. Q. Lin, *Anal. Chem.*, 2003, **75**, 324-331.

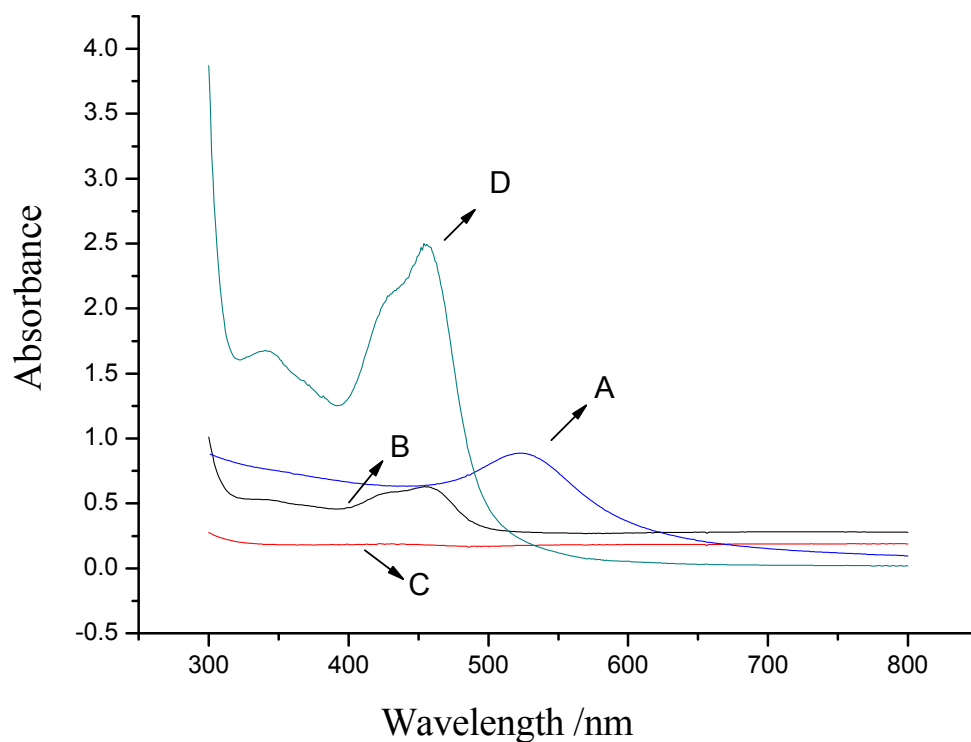


Fig. S1: UV/Vis absorption spectra of AuNPs synthesized with varying concentration of $\text{Ru}(\text{bpy})_2(\text{NH}_2\text{-phen})^{2+}$: 0.25 mL NaBH_4 (0.075 %, w/w, 0.020 mol L^{-1}) was added into the mixture of 20 mL HAuCl_4 (0.01 %, w/w) and 0.1 mL 50 mM (curve D), 10 mM (curve B), 1 mM (curve C) and 0.1 mM (curve A) $\text{Ru}(\text{bpy})_2(\text{NH}_2\text{-phen})^{2+}$.

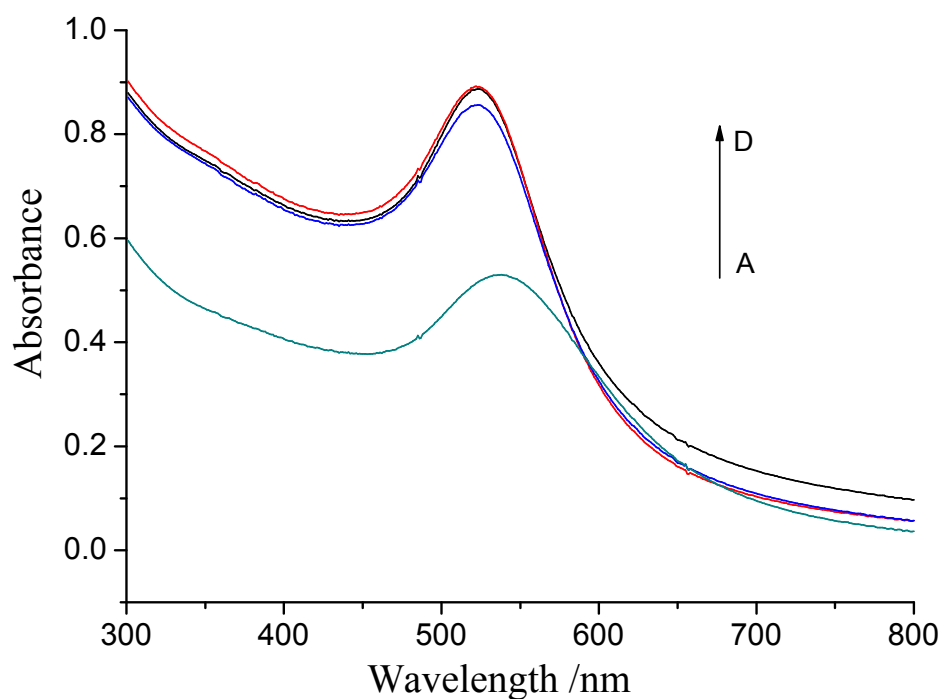


Fig. S2: UV/Vis absorption spectra of AuNPs synthesized with varying amounts of NaBH_4 (0.075 %, w/w): 0.1 (curve A), 0.25 (curve B), 0.5 (curve C), 1 mL (curve D) NaBH_4 was added into the mixture of 20 mL HAuCl_4 (0.01%, w/w) and 0.1 mL $\text{Ru}(\text{bpy})_2(\text{NH}_2\text{-phen})^{2+}$ (0.1 mM). The maximum absorption wavelength is approximately 520 nm.