Electronic Supplementary Material (ESI) for Analyst

Supporting Information for

Stable fluorescent gold nanoparticles for detection of Cu^{2+} with good sensitivity and selectivity

Yongming Guo,[a,b,c] Zhuo Wang,*[b] Huawu Shao*[a] and Xingyu Jiang*[b]

[a] Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu, Sichuan, 610041, China. Fax: (+86)28-85222753; Tel: (+86)28-85356511; E-mail: shaohw@cib.ac.cn

[c] National Center for Nanoscience and Technology, Beijing, 100190, China. Fax: (+86)10-82545631; Tel: (+86)10-82545575; E-mail: wangz@nanoctr.cn, xingyujiang@nanoctr.cn

[c] Graduate University of Chinese Academy of Sciences, Beijing, 100049, China

Experimental Section

Materials

11-mercaptoundecanoic acid (11-MUA), 3-mercaptopropanoic acid (3-MPA) and 16-mercaptohexadecanoic acid (16-MHA) were obtained from Sigma Aldrich. Chloroauric acid ($HAuCl_4$) was purchased from the Shenyang Jinke Reagent Company (Shenyang, China). Sodium borohydride ($NaBH_4$) were purchased from Tianjin Chemical Reagent Company. Methanol was bought from Beijing Chemical Reagent Company. Other reagents and chemicals were all of analytical reagent grade. Water was from a Milli-Q system.

Synthesis of fluorescent gold nanoparticles (11-MUA-AuNPs)

The 11-MUA-AuNPs were synthesized through the reduction of $HAuCl_4$ by $NaBH_4$ with 11-MUA as the protecting group in methanol solutions based on the reported procedures with some modifications.[s1] Briefly, 11-MUA (about 23 mg) was firstly dissolved in methanol (10 mL) in a flask and the solution was stirred for about 10 min in an ice bath. Then, about 0.515 mL $HAuCl_4$ (40 mg/mL in methanol) was rapidly added to the solution under vigorous stirring. The molar ratio of 11-MUA: Au^{3+} was about 2:1 and the mixture was stirred for about 20 min. Subsequently, 2.5 mL 0.2 M of $NaBH_4$ in cool methanol solutions was rapidly added into the above mixture under vigorous stirring. The solutions became dark-brown at once, indicating the formation of gold nanoparticles. The mixture was allowed to proceed for about 1 hour, methanol was removed under pressure and the residues were dissolved in about 10 mL water. The purification of the fluorescent 11-MUA-AuNPs was conducted with a dialysis membrane (14 KDa, MW. cutoff, Millipore) for about 24 hours in the dark. The procedures of the synthesis of 3-MPA and 16-MHA-protected gold nanoparticles were similar with the above synthetic procedure.

Instrumentation

A. UV-vis spectroscopy

Ultraviolet-visible (UV-vis) absorption spectra were measured using Shimadzu UV-2450 spectrophotometer.

B. Fluorescence spectroscopy

Fluorescence excitation and emission spectra were obtained in a microcell with 1 cm path length using a Perkin-Elmer LS55 luminescence spectrometer. The band pass for excitation and emission was set as 5 nm.

C. Fluorescence life

The fluorescence lifetime of 11-MUA-AuNPs was measured with an Edinburgh FL 900 single photo counting fluorescence life time instrument using H_2 lamp.

D. Quantum Yield

The quantum yield (QY) of the 11-MUA-AuNPs was measured using Rhodamine 6G (in ethanol) as a reference.

E. Fourier-transform infrared (FT-IR) spectra

FT-IR spectra were performed with a Perkin Elmer Spectrum One instrument. KBr

crystals were used as the matrix for sample preparation.

F. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were collected with a Tecnai G^2 20 S-TWIN transmission electron microscope operated at an acceleration voltage of 200 kV. The TEM specimens were prepared by placing one drop of a diluted solution on carbon coated copper grid and were dried at room temperature.

G. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on the Diamond TG/DTA (Perkin-Elmer) instrument. The bulk samples were obtained by freeze-drying of purified 11-MUA-AuNPs on (FD-1, Beijing Boyikang Experimental Instrument Co., Ltd., Beijing, China). The dry samples were placed in an alumina crucible under flowing nitrogen. The data was collected from room temperature to 800 ^{o}C at a heating rate of 10 $^{o}C \cdot min^{-1}$.

H. X-ray photoelectron spectroscopy (XPS)

The photoelectron spectra of the samples were obtained using an X-ray photoelectron spectrometer (Perkin-Elmer, PHI-5300). The Samples were prepared by repeatedly dropping the purified 11-MUA-AuNPs solution on silicon slice and allowed to dry in oven. The binding energies were calibrated with C 1s (284.8 eV).

I. X-ray diffraction (XRD)

XRD patterns were recorded on a Rigaku D/max-2500B2+/PCX system using Cu Kα radiation (λ = 1.5406 Å).

J. Photostability

Photostability tests were performed at room temperature. The 11-MUA-AuNPs solution was placed in a vial. The light of 254 nm from a 12 W ultraviolet lamp (ZF-7, Gongyi City Yuhua Instrument Co., Ltd., Henan Province, China) was employed to excite the 11-MUA-AuNPs. The light source (from a 254 nm) was placed 10 cm away from the vial. The fluorescence intensity of the 11-MUA-AuNPs was measured every 20 min.

Supporting Figures

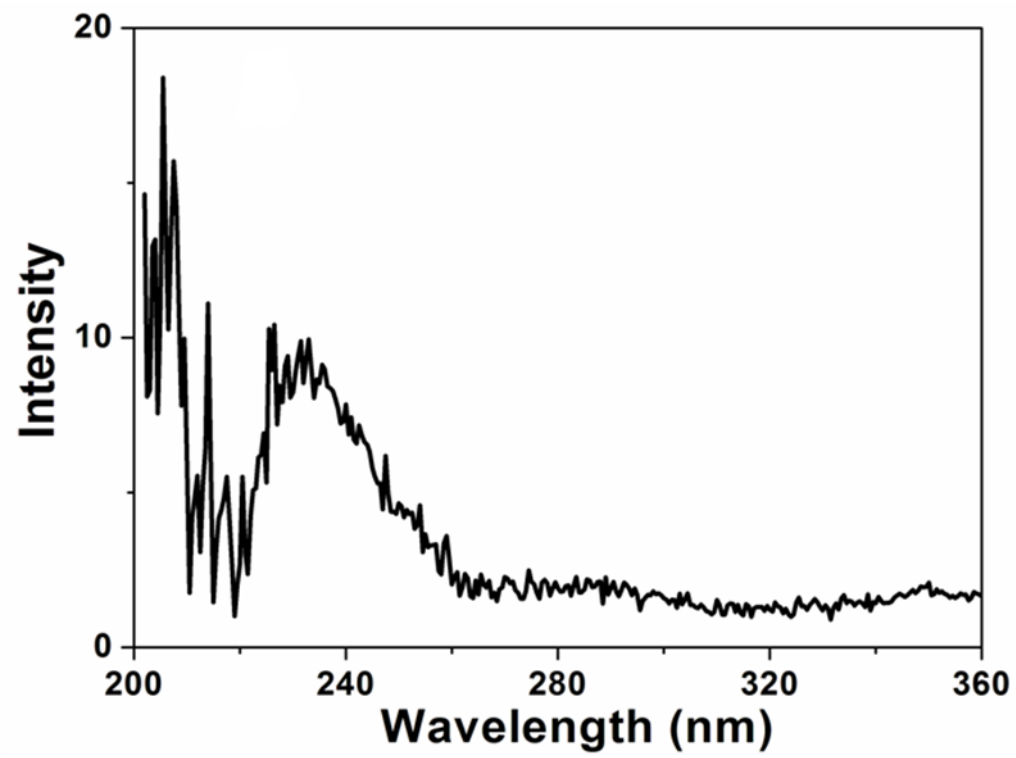

Fig. S1. Excitation spectrum of 11-MUA-AuNPs.

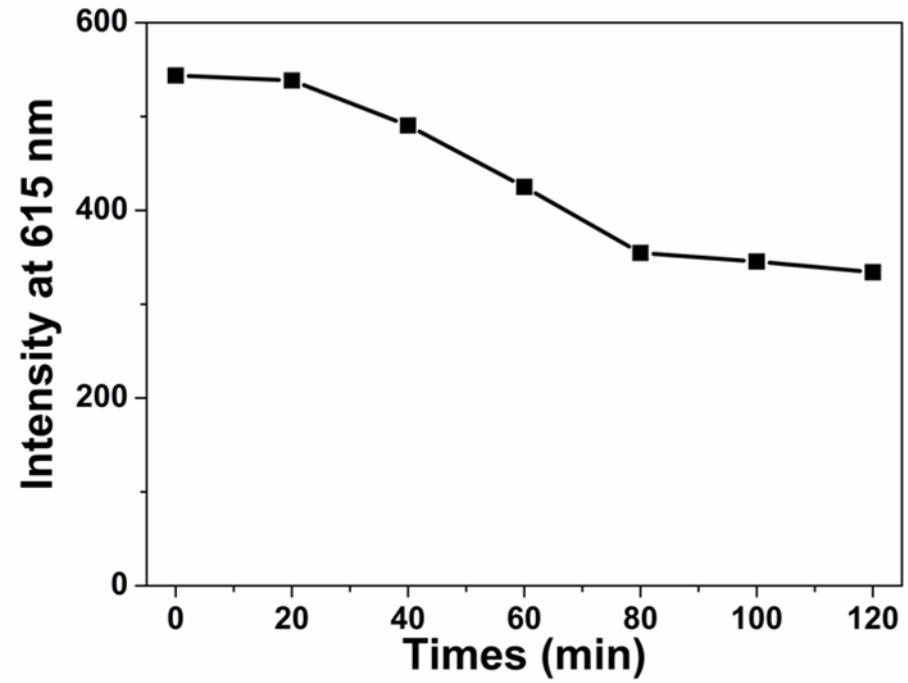

Fig. S2. Photostablility of 11-MUA-AuNPs measurement. Fluorescence intensity of 11-MUA-AuNPs at 615 nm during 120 min of UV irradiation (λ_{ex} = 250 nm).

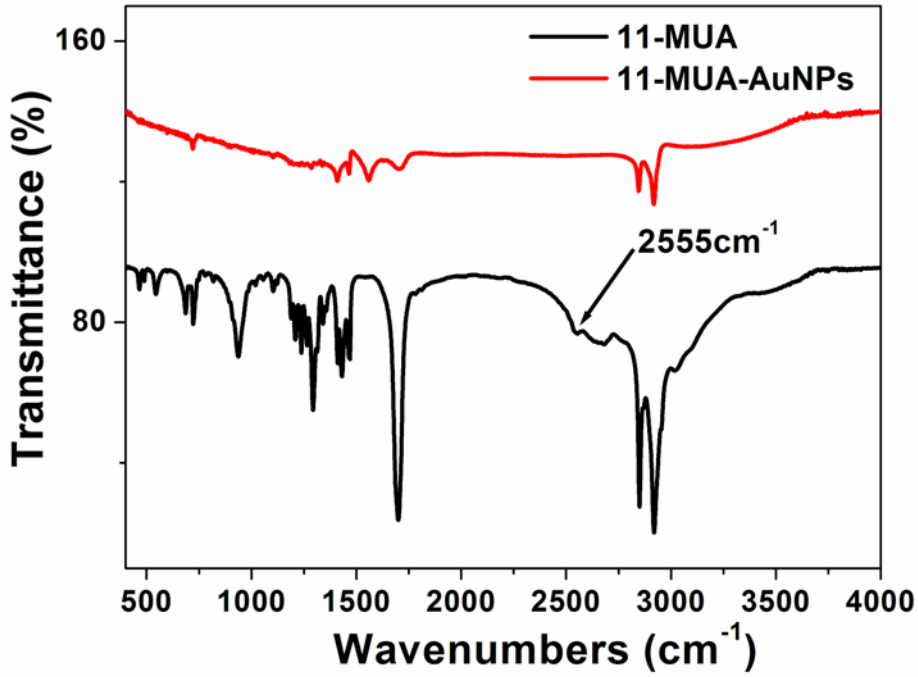

Fig. S3. FT-IR spectra of free 11-MUA (black) and 11-MUA-AuNPs (red). The S-H stretching feature was about 2555 cm^{-1}.

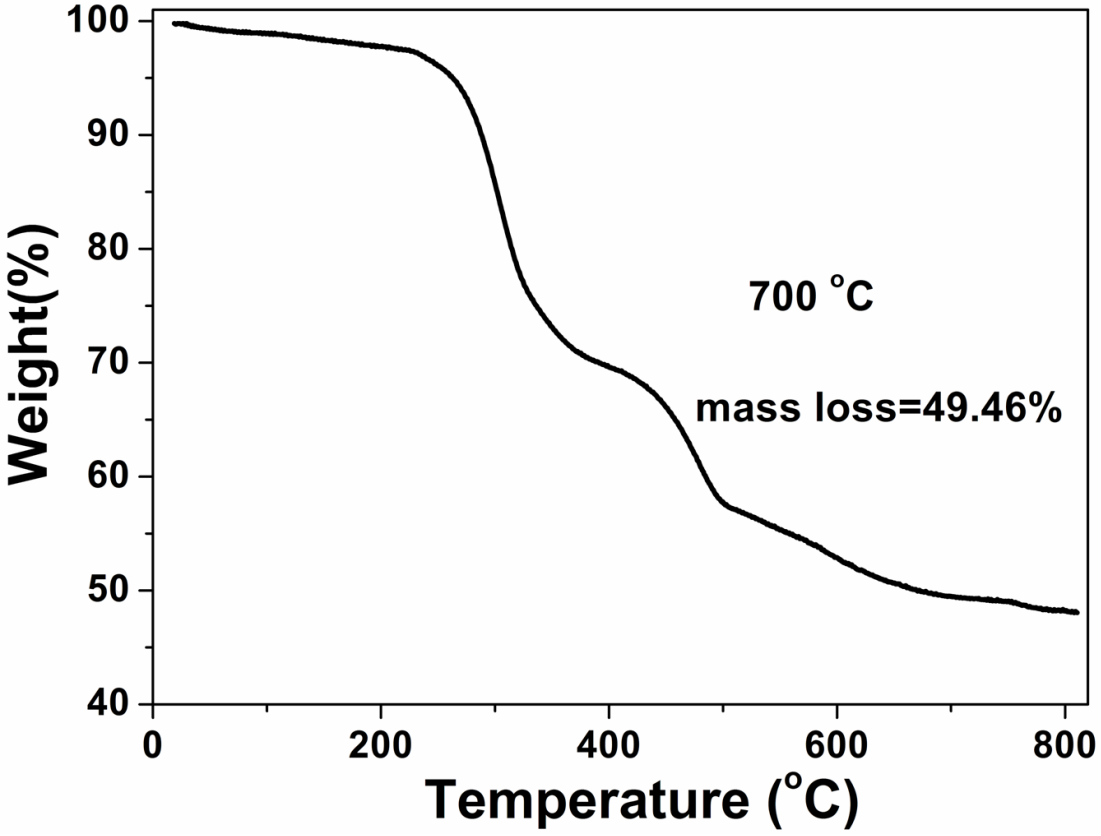

Fig. S4. TGA thermogram of 11-MUA-AuNPs with a heating rate of 10 ^{o}C/min.

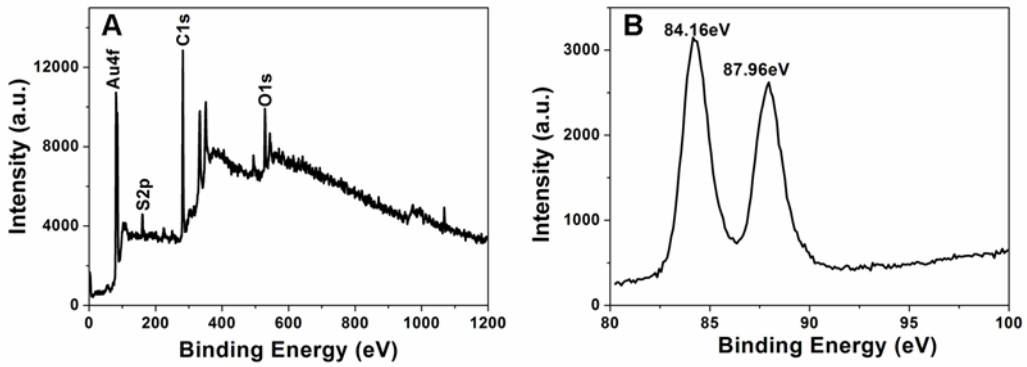

Fig. S5. (A) XPS spectrum of 11-MUA-AuNPs and (B) its expanded spectrum of Au_{4f}.

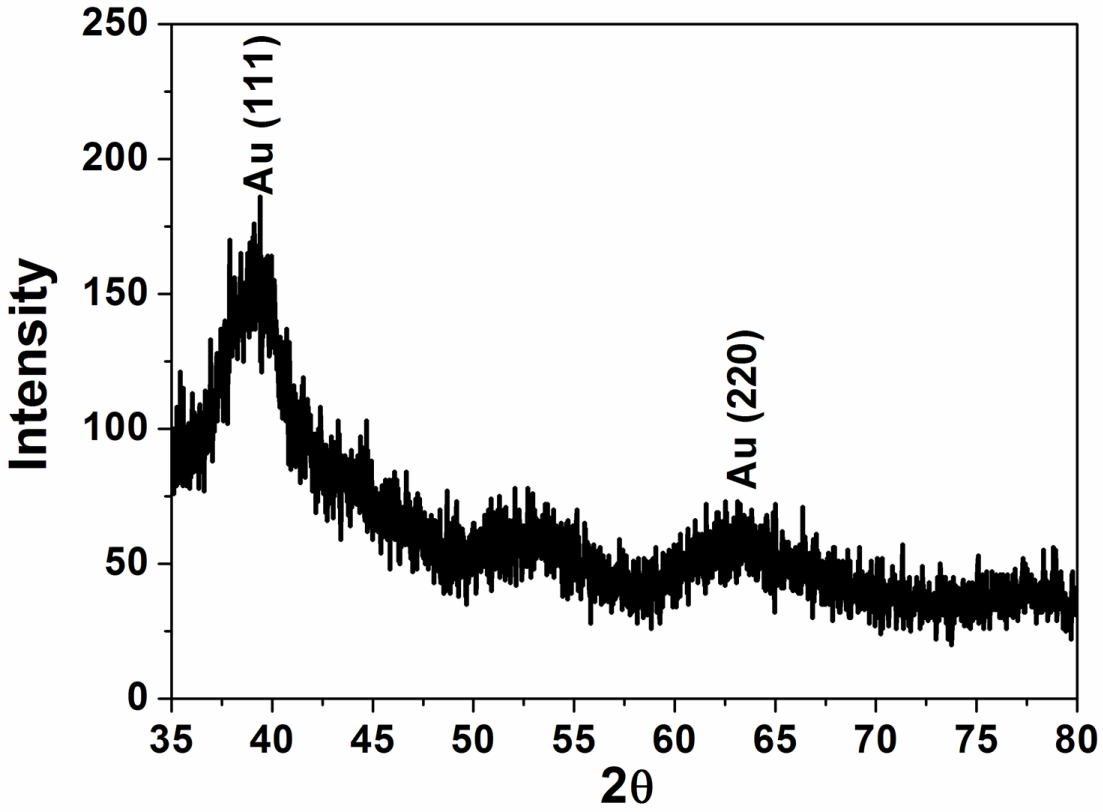

Fig. S6. Powder XRD pattern of 11-MUA-AuNPs.

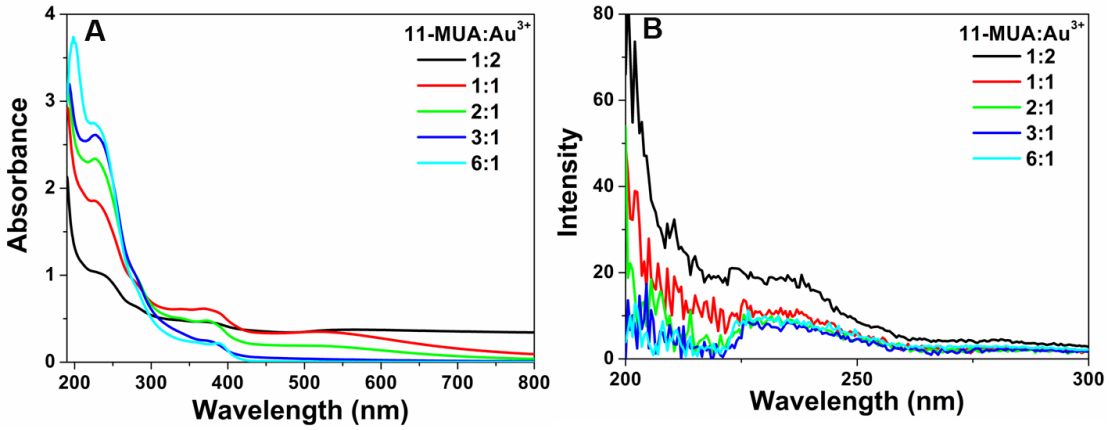

Fig. S7. UV-vis absorption spectra (A) and excitation of spectra (B) of 11-MUA-AuNPs synthesized from different ratios of 11-MUA and Au^{3+} (λ_{ex} = 250 nm).

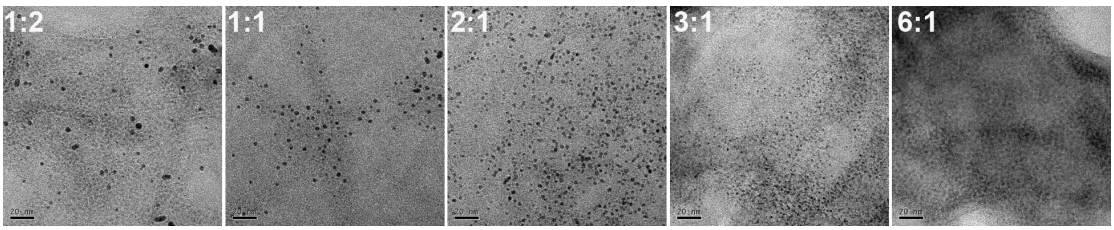

Fig. S8. TEM images of 11-MUA-AuNPs synthesized from different ratios of 11-MUA and Au^{3+}.

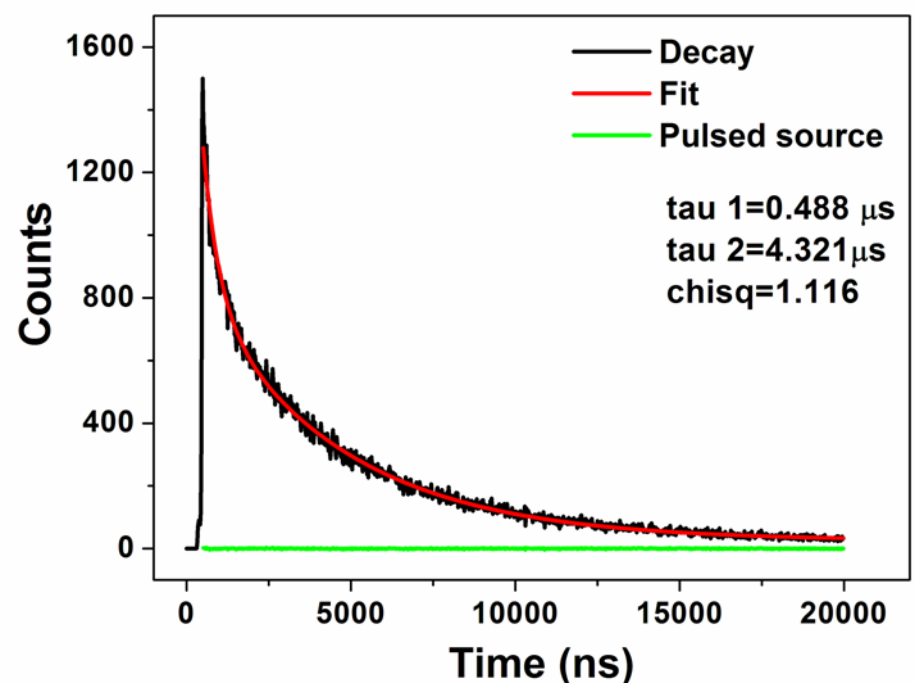

Fig. S9. Fluorescence lifetime of 11-MUA-AuNPs measurement. The solid line

gives a 2-exponential fit (λ_{ex} = 250 nm).

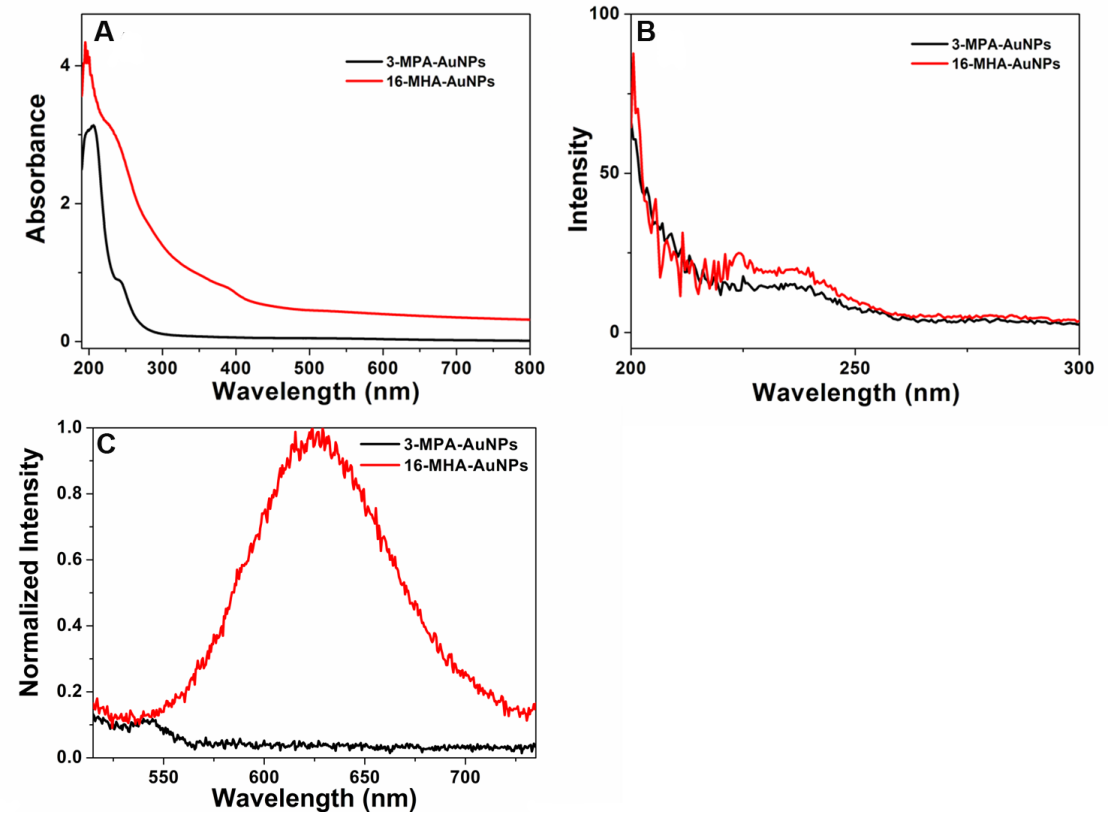

Fig. S10. UV-vis absorption spectra (A), excitation of spectra (B) and emission spectra (C) of 3-MPA-AuNPs and 16-MHA-AuNPs (λ_{ex} = 250 nm). The quantum yield of 3-MPA-AuNPs and 16-MHA-AuNPs is 0 and 0.074%, respectively.

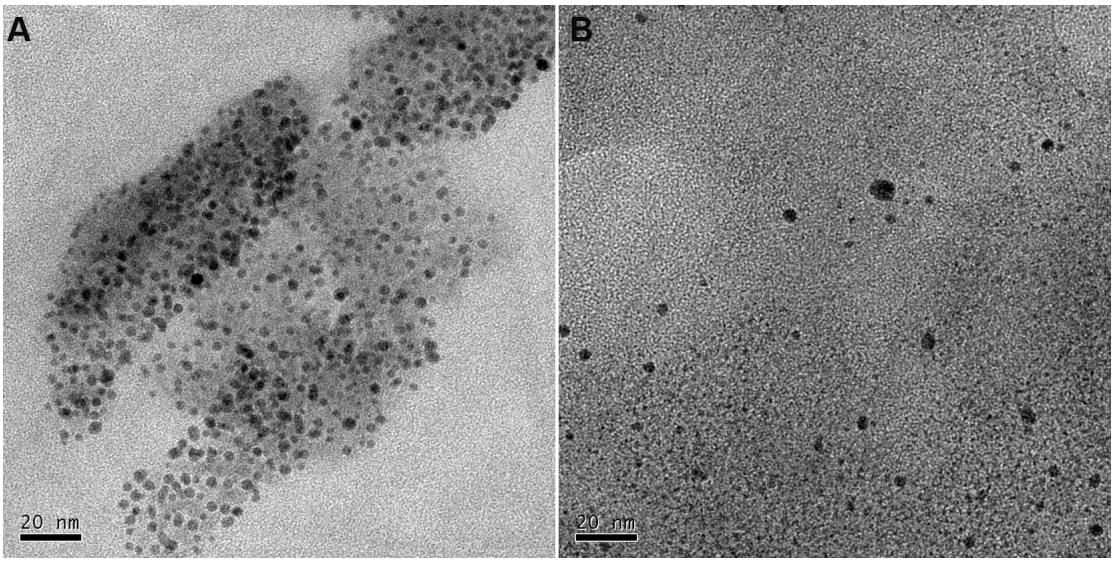

Fig. S11. TEM images of 3-MPA-AuNPs (A) and 16-MHA-AuNPs (B).

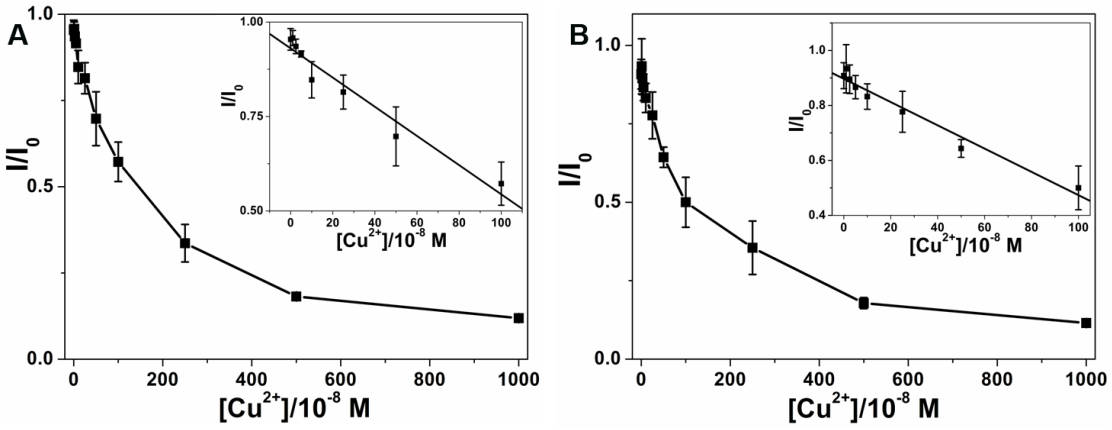

Fig. S12. Plot of the fluorescence intensity ratio of the 11-MUA-AuNPs at 615 nm versus the concentrations of Cu^{2+} in the tap water (A) and in the lake water (B) (performed in pH 7.0, 20 mM HEPES buffer; I_0 and I correspond to the fluorescence intensity of 11-MUA-AuNPs at 615 nm in the absence and presence of metal ions, respectively. λ_{ex} = 250 nm.).

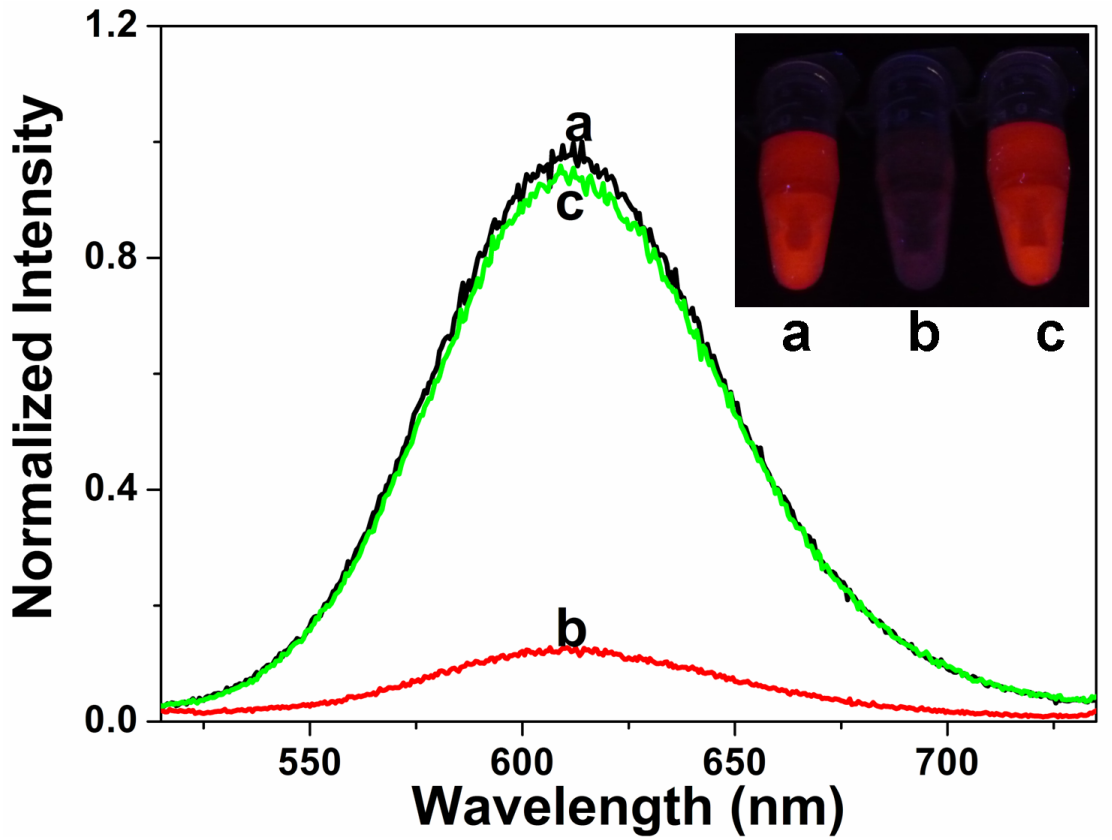

Fig. S13. Emission spectra of 11-MUA-AuNPs in the 20 mM HEPES buffer solution (pH = 7.0) (a), in the presence of 10 μM of Cu^{2+} (b), and in the presence of 10 μM of Cu^{2+} and 10 μM of EDTA (c) (λ_{ex} = 250 nm). The insert image is their corresponding photographs in the light of 254 nm.

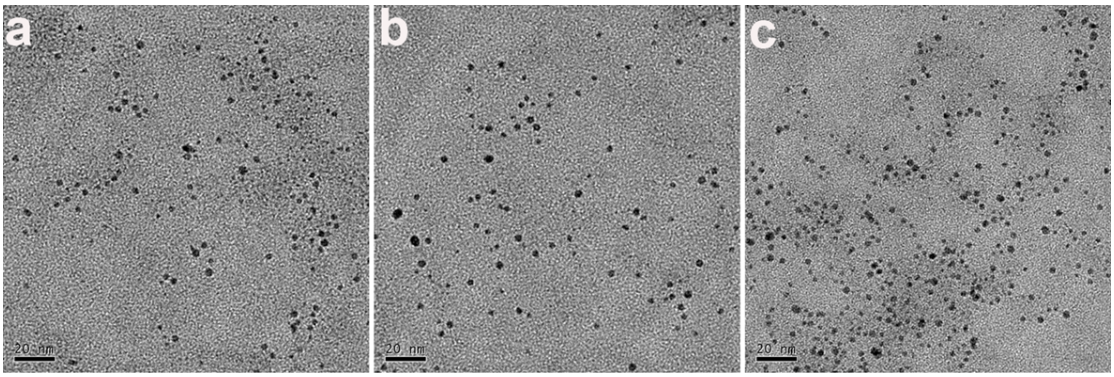

Fig. S14. TEM images of 11-MUA-AuNPs in the 20 mM HEPES buffer solution (pH = 7.0) (a), in the presence of 10 μM of Cu^{2+} (b), and in the presence of 10 μM of Cu^{2+} and 10 μM of EDTA (c).

s1 Y. Negishi, K. Nobusada and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 5261-5270.