

## Supporting Information

### Photoreductive Synthesis of Water-soluble Fluorescent Metal Nanoclusters

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#### Contents:

- SI-1: Synthesis and Characterization of Thioether Polymer Ligands.
- SI-2: Preparation and Characterization of Metal Nanoclusters.
- SI-3: References.

### SI-1: Synthesis and Characterization of Thioether Polymer Ligands.

*Materials:* All chemicals were of analytical grade and used as received without any further purification, unless otherwise described. Methacrylic acid, (MAA, 99%), copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ , 99%), silver nitrate ( $\text{AgNO}_3$ , 99%), hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ , 99%), Rhodamine B (Rh B), anhydrous ether, anhydrous ethanol, n-butanol, n-hexane, toluene, acetone, methanol, tetrahydrofuran (THF) N,N-dimethylformamide (DMF) were purchased from National Medicines Corporation Ltd. of China. Pentaerythritol tetrakis 3-mercaptopropionate (PTMP, 97%) was obtained from Aldrich.

#### *Synthesis of Functional Thioether Polymer Ligands:*

PTMP-PMAA: In a typical synthesis, 100 mL ethanol solution containing methacrylic acid monomer (20.000 g, 232 mmol), chain transfer agent PTMP (2.267 g, 4.64 mmol) and AIBN (0.190 g, 2.32 mmol) were added to a four-necked round-bottomed flask fitted with a reflux condenser under nitrogen with mechanical stirring. The temperature of the reaction mixture was maintained at 75 °C and refluxed for 5 h. The solvent was removed by rotary evaporator after the reaction. The viscous products were isolated by precipitating into cold anhydrous ether. The redundant solvent and monomer were removed by evaporation using a vacuum oven set at 45 degree for 24 h. A fraction of low molar mass polymer, unreacted monomer and some oligomers remained after reaction has been removed during the precipitation step. The yield of thioether polymer (PTMP-PMAA) was 16.749 g, 84%.

#### *Characterization of Polymer Ligands:*

GPC: Gel permeation chromatography (GPC) was performed using a Polymer Laboratories system equipped with a PL-ELS 1000 evaporative light scattering detector and a series of PC mix gel columns 5  $\mu\text{m}$  MIXED C and D. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. Calibration was carried out using EasiCal polystyrene standards (Polymer Laboratories). The polymer was first converted to the methyl ester using TMS-diazomethane reagent to render it soluble in THF. <sup>1</sup> The  $M_n$  and  $M_w$  of polymer ligand are 5400 and 7236 g/mol, respectively.

## SI-2: Preparation and Characterization of Metal Nanoclusters.

### *Preparation of Metal Nanoclusters (MNCs):*

In a typical experiment, a freshly prepared mixture solution of metal precursor (copper nitrate, silver nitrate and hydrogen tetrachloroaurate) and PTMP-PMAA were incubated for ca. 30 min until it become clear, then subjected to UV-irradiation at 365 nm for various time intervals.

### *Characterization of Metal Nanoclusters:*

**Photoluminescence (PL) Measurement:** The fluorescence of MNCs was acquired by the FP-6500 fluorescence spectrometer (Jasco, JPN) at the conditions of 25 °C and 46% humidity. The emission spectra were measured at 480 nm wavelength and the excitation spectra were measured at the corresponding maximum emission wavelength. The MNC aqueous solution (200 µL) was loaded into quartz cuvette for analysis.

**UV-visible Absorption Spectroscopy:** UV-visible spectra were carried out on a spectromax plus 384. The aqueous MNCs solutions (300 µL) were analyzed in a 1 cm path length quartz cuvette at room temperature.

**Transmission Electron Microscope (TEM).** Transmission electron microscopy images were recorded on a JEOL-2100 electron microscope operating at an acceleration voltage of 200 kV. TEM samples were prepared by dropping a diluted water solution of MNCs onto carbon-coated copper grids (400 mesh).

**MALDI-TOF.** Samples were analyzed on a Bruker Autoflex MALDI-TOF/TOF instrument. Samples (0.5 µL) were spotted to a MALDI target plate with 0.5 µL CHCA matrix (10 mg/mL CHCA in 50% ACN/0.1%TFA/25mM diammonium citrate) and externally calibrated with a mixture of angiotensin I (5 pmol/µL)/ACTH (5 pmol/µL)/insulin (100 pmol/µL) / cytochrome C (100 pmol/µL). Data was processed using FlexAnalysis (Bruker).

**X-ray Photoelectron Spectroscopy (XPS).** The XPS of Au NCs was measured by AXIS-ULTRA DLD high-performance imaging X-ray photoelectron spectroscopy (Shimadzu, Japan).

**Chemical photostability:** The effect of metal ions on the fluorescence of M NCs was investigated as follows. First, Cd<sup>2+</sup>, Al<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Au<sup>3+</sup>, Pt<sup>4+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup> nitrates or chlorides solutions (0.2 M) were prepared. Then the fluorescent M NCs were added into the each solution and the final concentration of M NCs is 0.1 mM. The fluorescence of mixtures were immediately measured using FP-6500 fluorescence spectrometer (Jasco, JPN) equipped with a high-power Xenon lamp.

**Quantum Yield (QY) Measurement:** The photoluminescence quantum yield of a compound is defined as the fraction of molecules that emit a photon after direct excitation by the source.<sup>2</sup> This quantity is not the same as the total number of emitted photons which escape a bulk sample divided by the total number of absorbed photons, although in many instances the two quantities are nearly equal. The measurement of quantum yield was employed the compared method which is described below (Equation 1):

$$\Phi_{unk} = \frac{A_{std}}{A_{unk}} \times \frac{F_{unk}}{F_{std}} \times \frac{n_{unk}^2}{n_{std}^2} \times \Phi_{std} \quad (1)$$

$\Phi$  = Quantum Yield; unk = Unknow Sample; std = Standard; n = Refractive index of solvent; A = Absorption at the selected excitation wavelength; F = Integrated fluorescence signal in the emission region. To calculate the quantum yield of MNCs protected by polymer ligands, a series of the samples and the standard Rhodamine B ( $\Phi = 0.95$ ) were measured. All the samples were diluted to ensure the optical densities less than 0.02 measured by Lambda 35 UV-Visible spectrophotometer (Perkin-Elmer, USA.) in order to reduce the error. The emission spectra were recorded on FP-6500 fluorescence spectrometer (Jasco, JPN) under the excitation of 405 nm light for Ag NCs and 360 nm light for Cu and Au NCs.

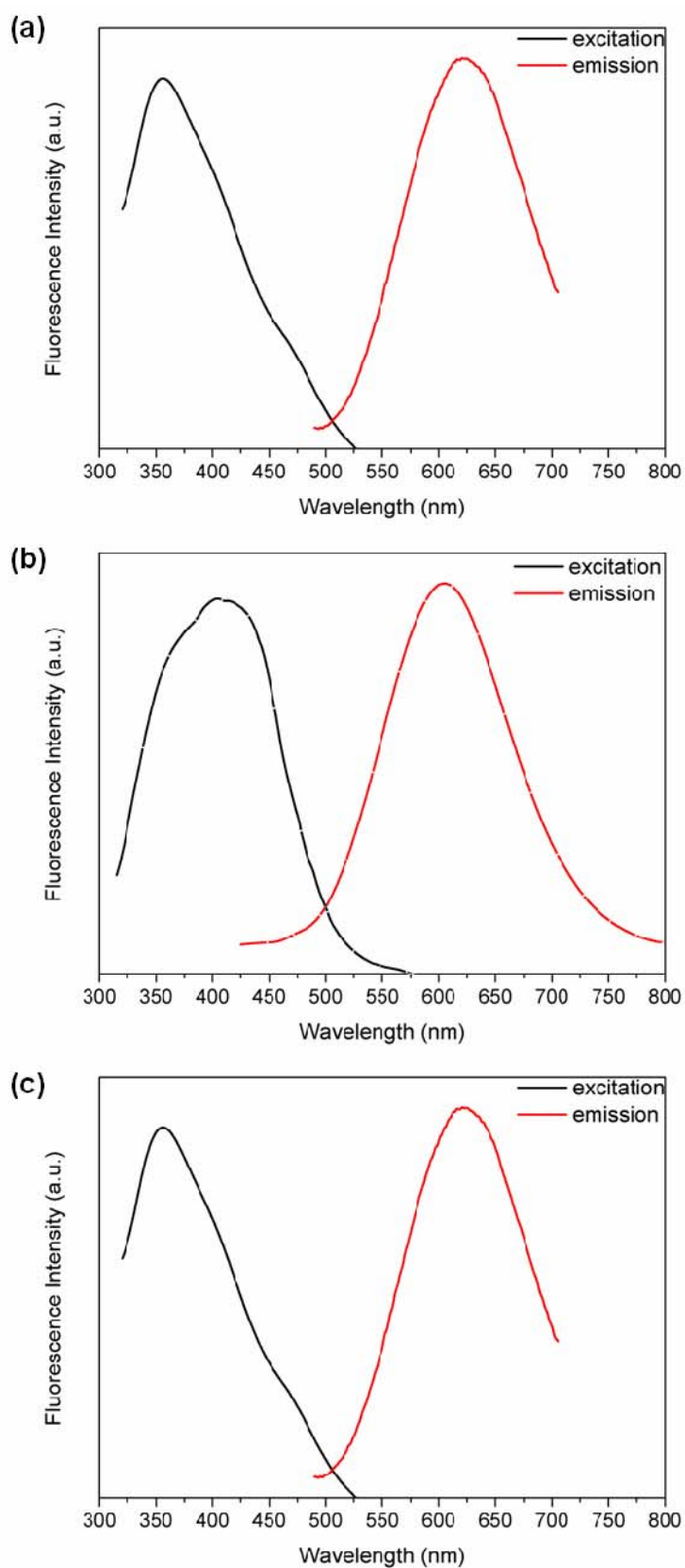


Figure S1. Photoluminescence emission and excitation spectra of (a) Cu NCs@PTMP-PMAA (b) Ag NCs@PTMP-PMAA (c) Au NCs@PTMP-PMAA. Their emissions are located at 630 nm, 605 nm, 610 nm, respectively.

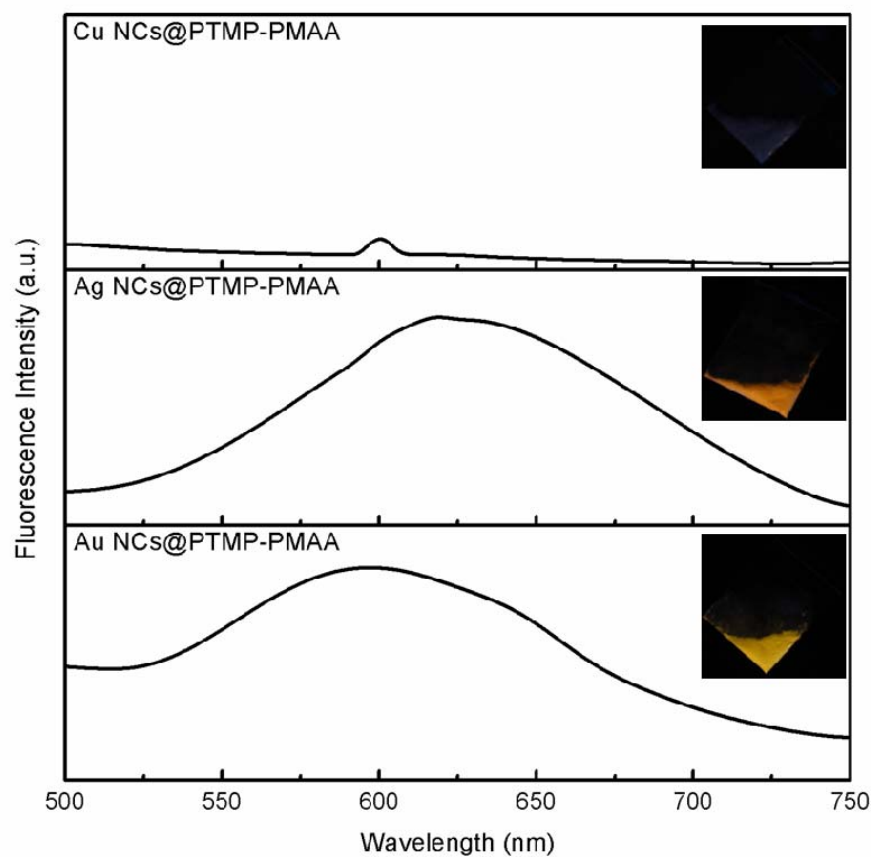


Figure S2. The emission spectrum of MNC powders and their photo images under the UV light.

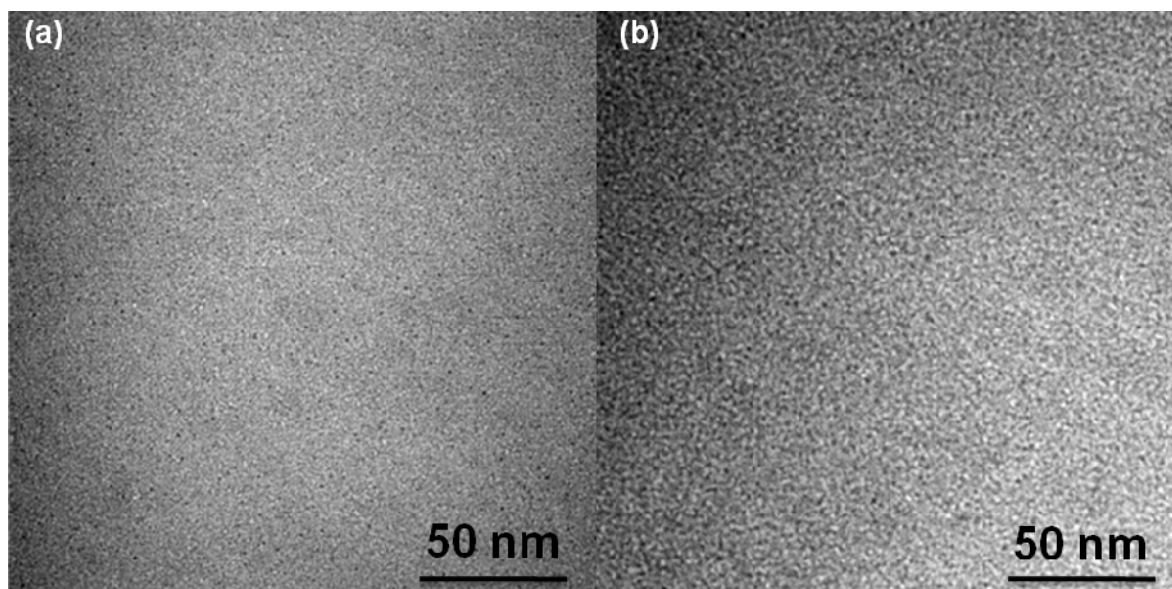


Figure S3. TEM images of PTMP-PMAA stabilized Cu NCs (a), Ag NCs(b).

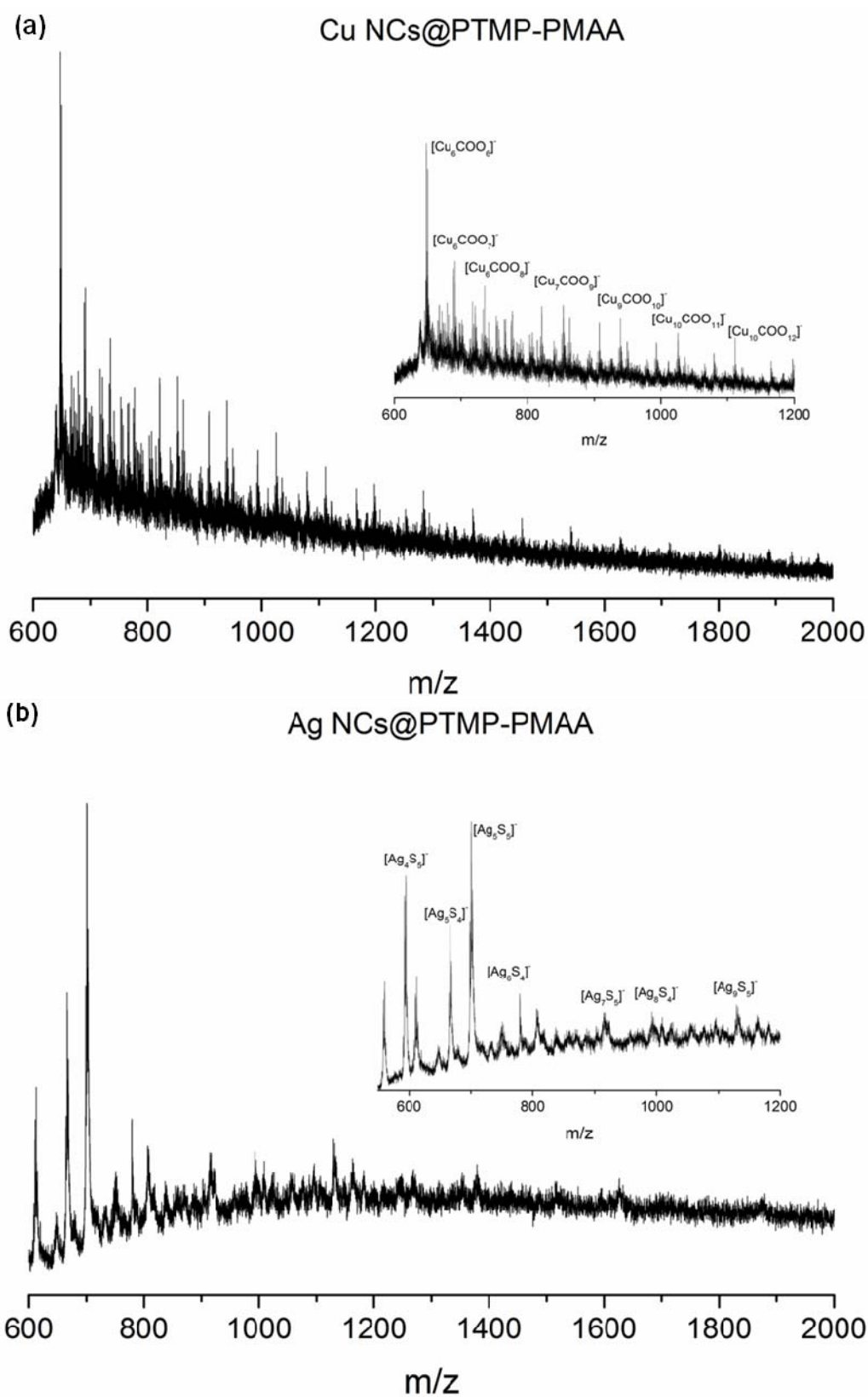


Figure S4. MOLDI-TOF spectra of PTMP-PMAA stabilized Cu NCs (a), Ag NCs(b).

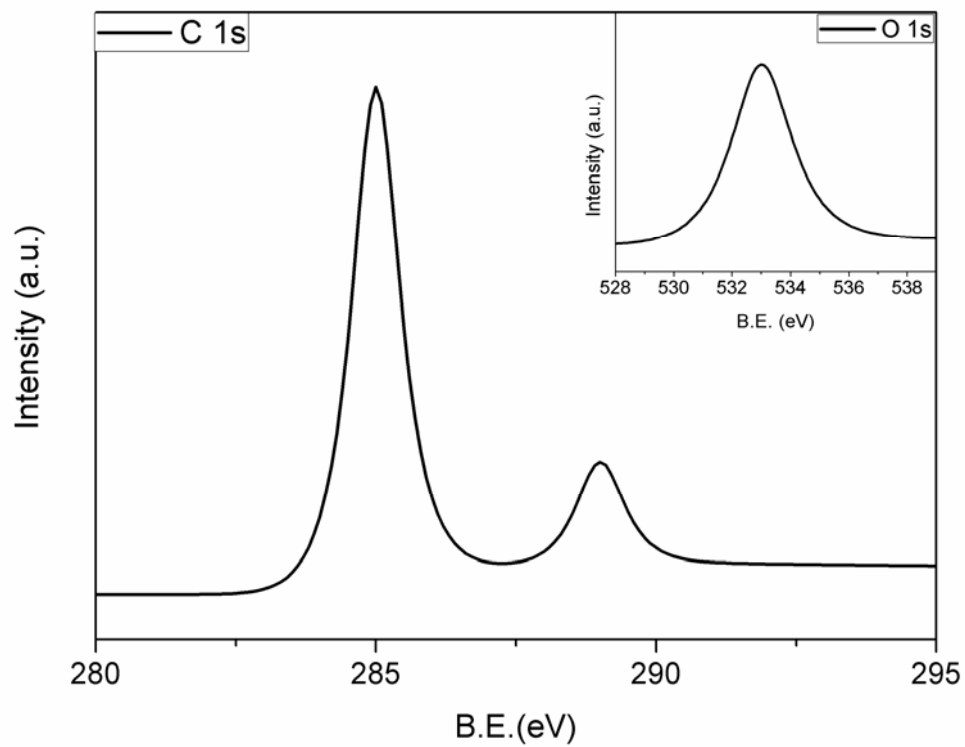


Figure S5. Binding energies of C 1s, O 1s (inset) in Au NCs.



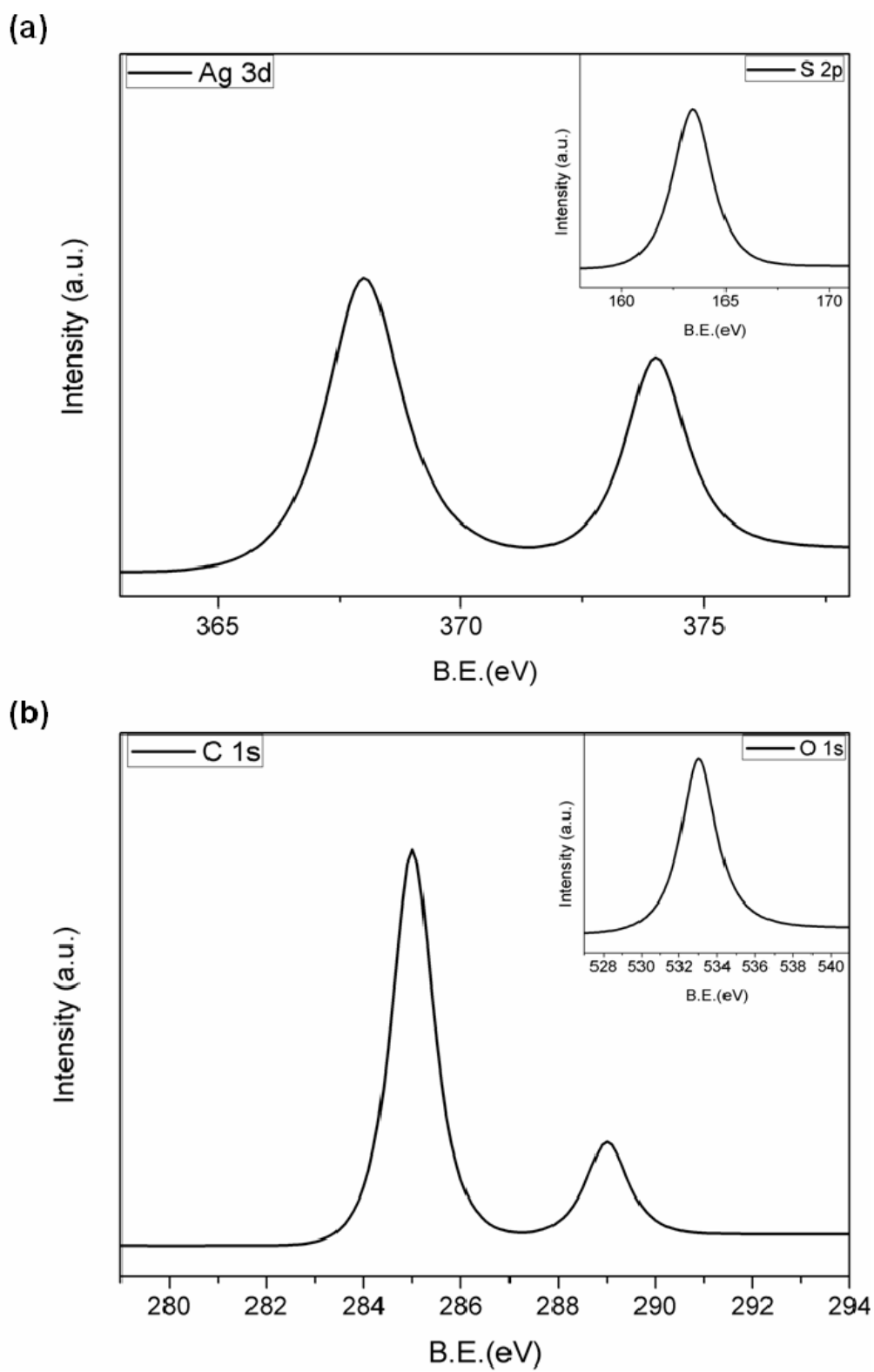


Figure S6. Binding energies of C 1s, O 1s (inset) in Ag NCs

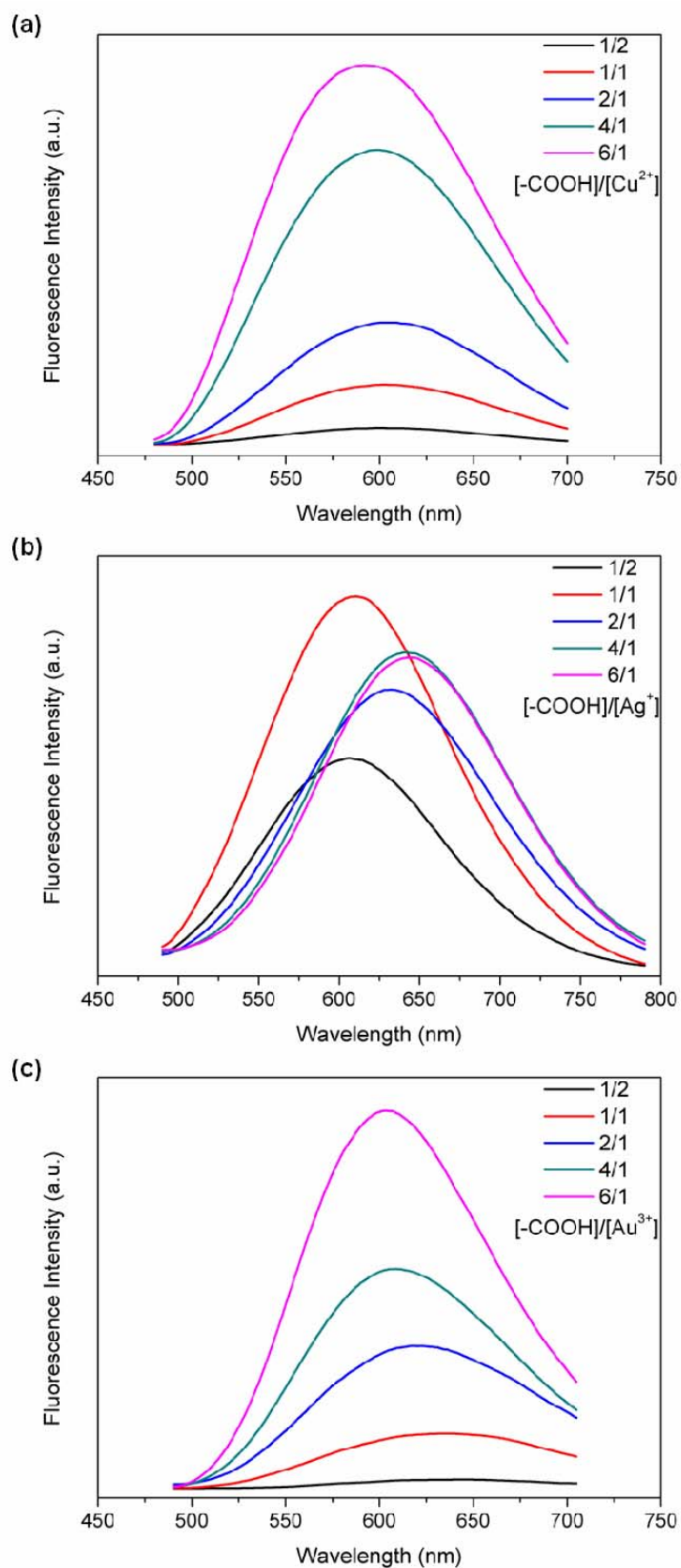


Figure S7. Fluorescence emission spectra of (a) Cu NCs (b) Ag NCs (c) Au NCs prepared from different [-COOH]/[M] ratios ranging from 1/2 to 6/1 under equal irradiation condition.

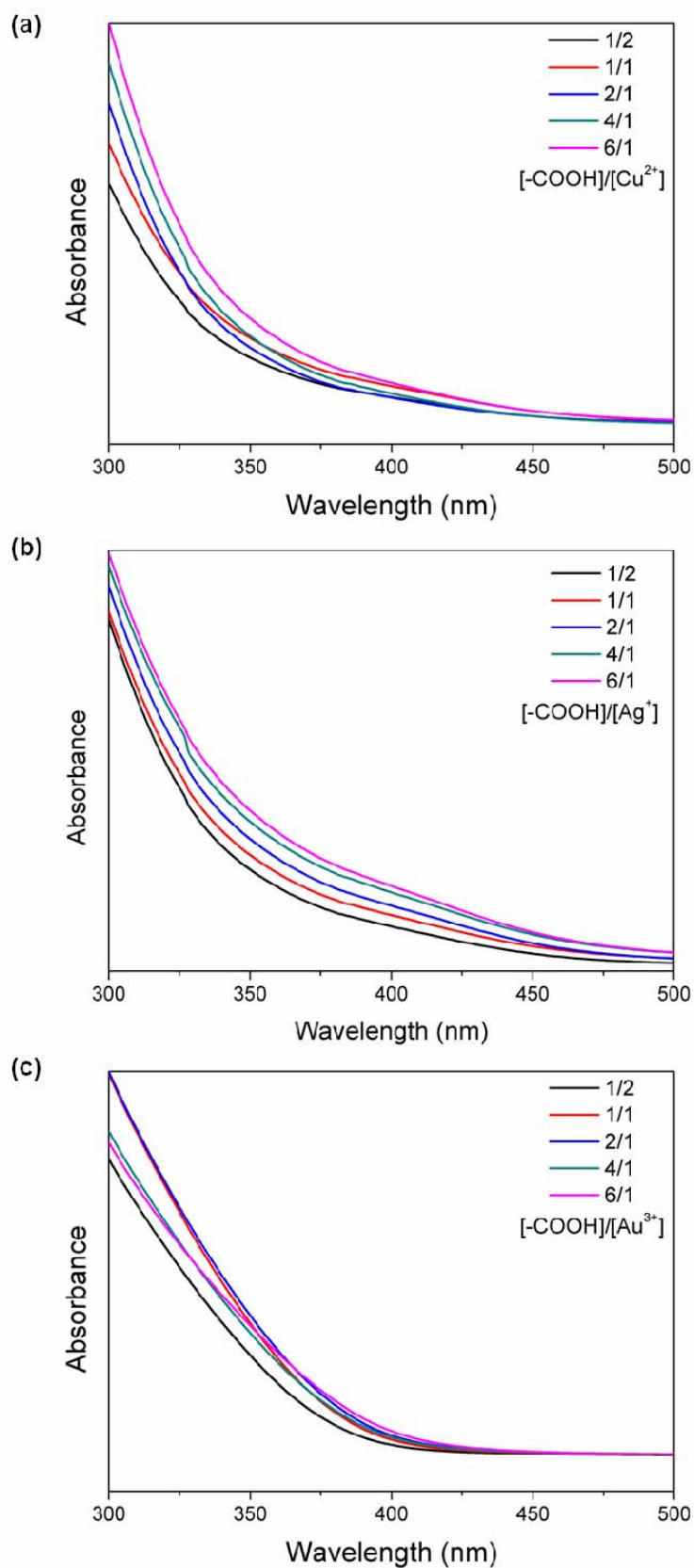


Figure S8. UV-vis absorption spectra of (a) Cu NCs (b) Ag NCs (c) Au NCs prepared from different [-COOH]/[M] ratios ranging from 1/2 to 6/1 under equal irradiation condition

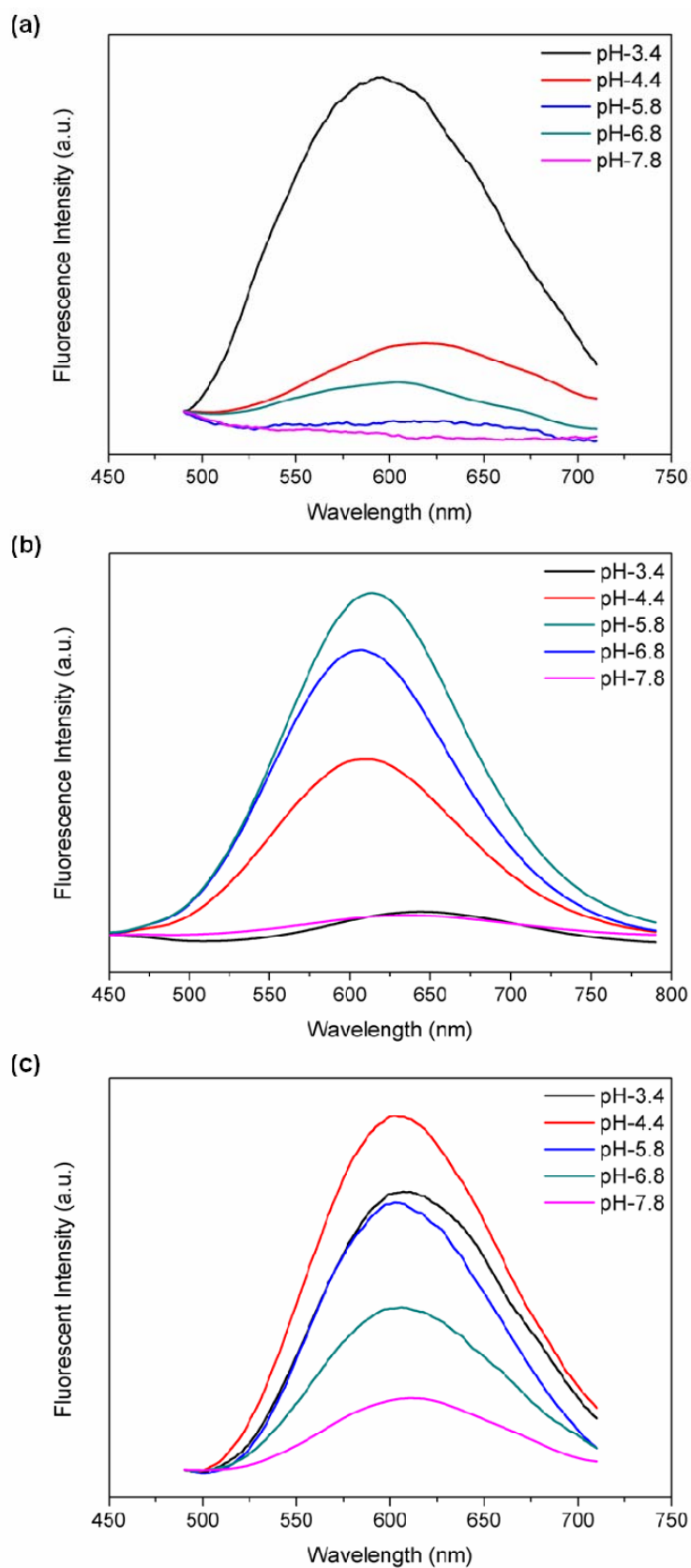


Figure S9. Fluorescence emission spectra of (a) Cu NCs (b) Ag NCs (c) Au NCs produced at different pH values. The emission spectra were all recorded upon irradiation at 365 nm for the same time.

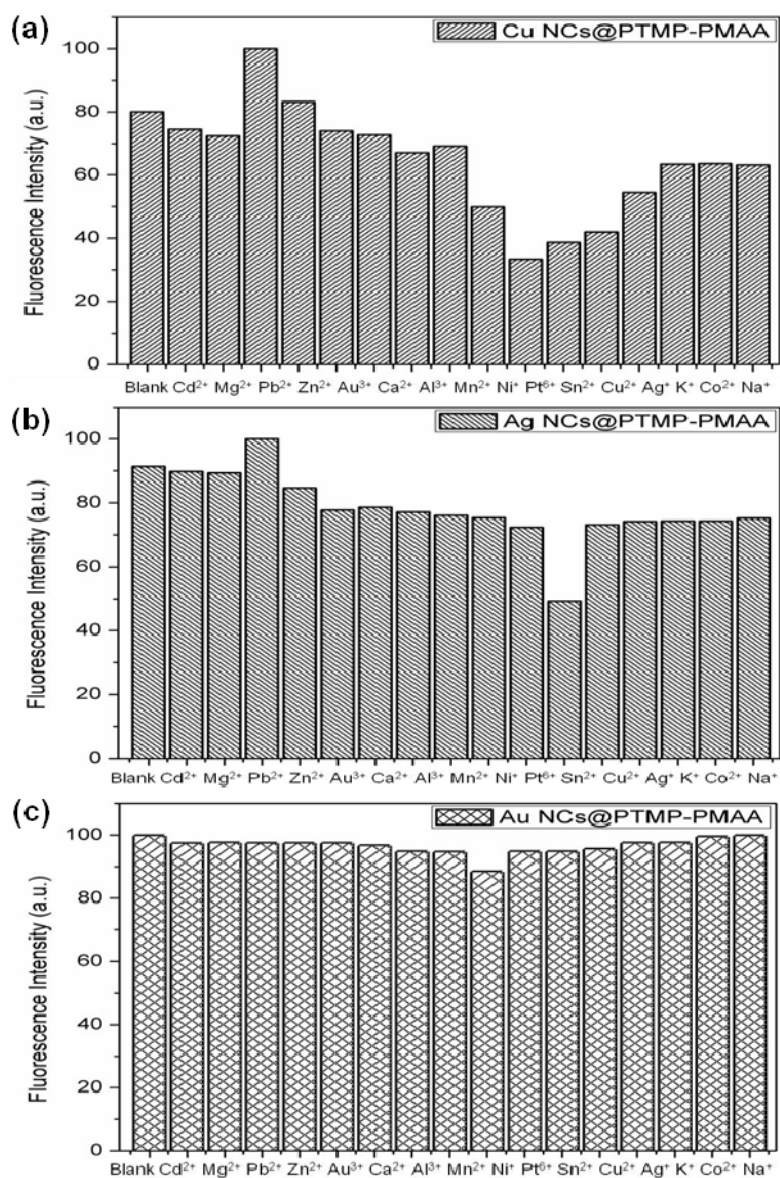


Figure S10. The histogram of fluorescence of (a) Cu NCs (b) Ag NCs (c) Au NCs in different metal ion solutions.

### SI-3: References

- (1) (a) Hussain, I.; Graham, S.; Wang, Z.; Tan, B.; Sherrington, D. C.; Rannard, S. P.; Cooper, A. I.; Brust, M. *J. Am. Chem. Soc.* **2005**, *127*, 16398; (b) Sherrington, D. C.; Bonner, P. *Polym. Commun.* **1984**, *25*, 71.
- (2) Crosby, G. A.; Demas, J. N. *J. Phys. Chem. A* **1971**, *75*, 991.