Supporting information

Cooperative binding of Bifunctionalized and Click Synthesized Silver Nanoparticles for Colorimetric Co^{2+} Sensing

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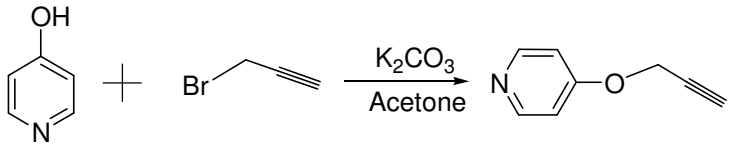
General procedure for the synthesis of 4-(prop-2-ynyloxy)pyridine: A suspension of 4-hydroxy pyridine (0.57 g，6 mmol) and anhydrous potassium carbonate (1.66 g, 12 mmol) in acetone (20 mL) was stirred for 0.5 h at room temperature. Then a solution of 3-bromopropyne (1.3 mL, 12 mmol) dissolved in acetone (5 mL) was slowly added. The reaction mixture was stirred for 2 h at 50 ℃. The cooled reaction mixture was filtered and washed with acetone. The filtrate were removed under vacuum and the residue was further purified by column chromatography eluting with ethyl acetate/methanol (v/v = 5:1); Yield: 90%. ^{1}HNMR(600 MHz, $CDCl_3$): δ 7.45 (d, *J*=7.2 Hz, 2H), 6.42 (d, *J*=7.2 Hz, 2H), 4.60 (s, 2H), 2.65 (s,1H).



Scheme 1 Synthesis of 4-(prop-2-ynyloxy)pyridine

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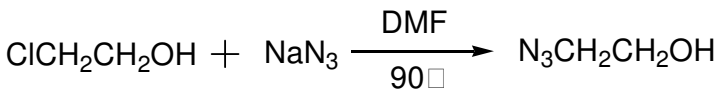
General procedure for the synthesis of 2-azidoethanol: A suspension of 2-chloroethanol (1.61 g, 0.02mol) and NaN_3 (2.60 g, 0.04 mmol) in DMF (20 mL) was stirred for 5 h at 50 ℃. The mixture was cooled and then diluted with ethyl acetate (20 mL) and washed with water (3 × 10 mL). The organic phase was dried over magnesium sulphate, filtered and the solvent was removed under reduced pressure. The azide was sufficiently pure to use without further work up; IR 3, *2110(-N_3)*, 2935, 2874 cm^{-1} (-CH_2-).



Scheme 2 Synthesis of 2-chloroethanol

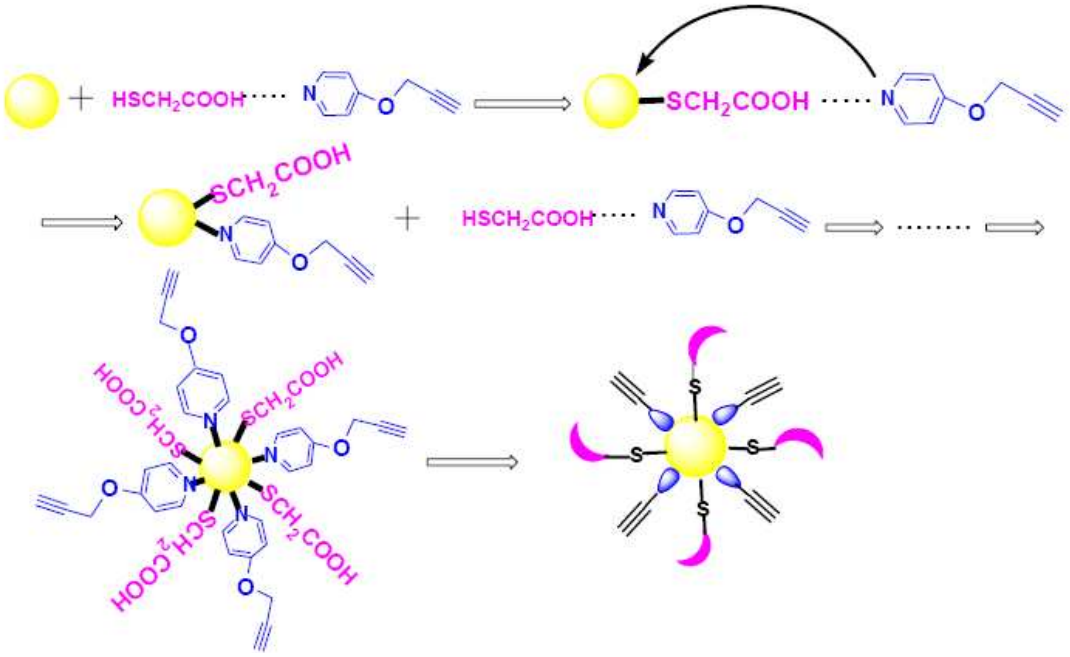


Figure.S1 Scheme of the arrangement between thioacetic acid and 4-(prop-2-ynyloxy)pyridine molecules.

Preparation of triazole-Ag NPs: 100 mL of silver nitrate ($AgNO_3$, 1.0 mL, 10^{-2} M) aqueous solution of was reduced by sodium borohydride (12mg) at room temperature to yield yellow colloidal silver particles. 4-(prop-2-ynyloxy) pyridine aqueous solution (1.0 mL, 10^{-3} mol/L) were added into above solution, stirring for 2h at room temperature. Alkynyl-Ag NPs were obtained in water. 2-azidoethanol (1.0 mL, 10^{-3} mol/L) was added into alkynyl-Ag NPs solution, stirring for 10 mins. Finally, the mixture of copper sulfate (10^{-6} M) and sodium ascorbic acid (10^{-7} M) were added into pyridine Ag NPs solution, stirring for 3h at 60 ℃. The mixture has been placed into high intensity ultrasound bath for 10 mins. The synthesized triazole-Ag NPs were purified by repeating centrifugation and redispersion in water. The finally dispersed triazole-Ag NPs can be used for metal ions detection.

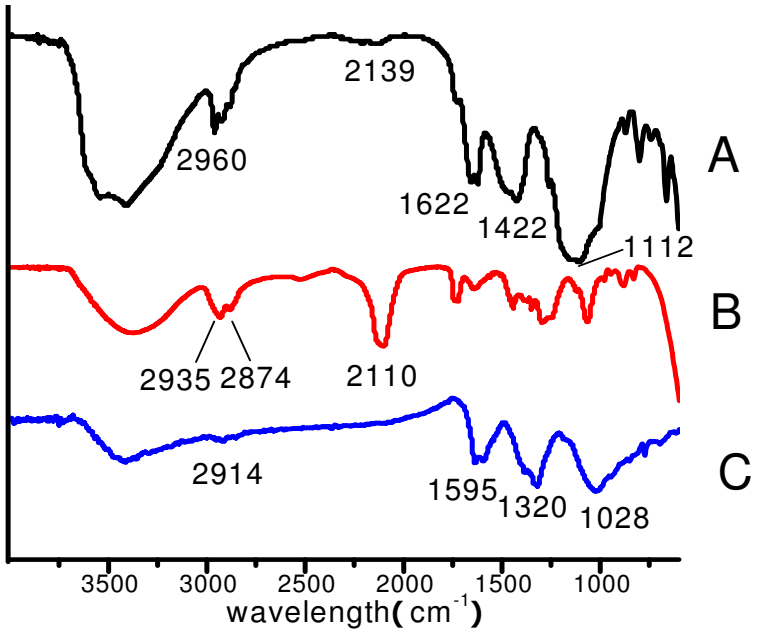


Figure.S2 FT-IR spectra of (A) alkynyl-Ag NPs (B) 2-azidoethanol (C) triazole-Ag NPs

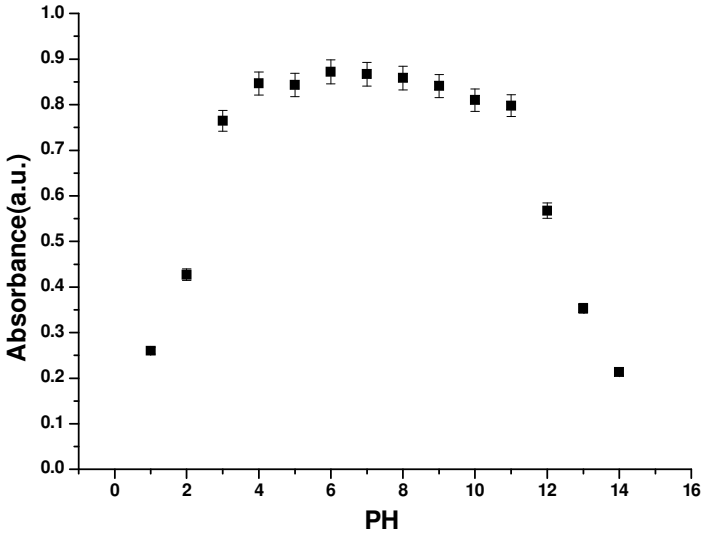


Figure. S3 Effect of pH on the triazole-carboxyl Ag NPs solution

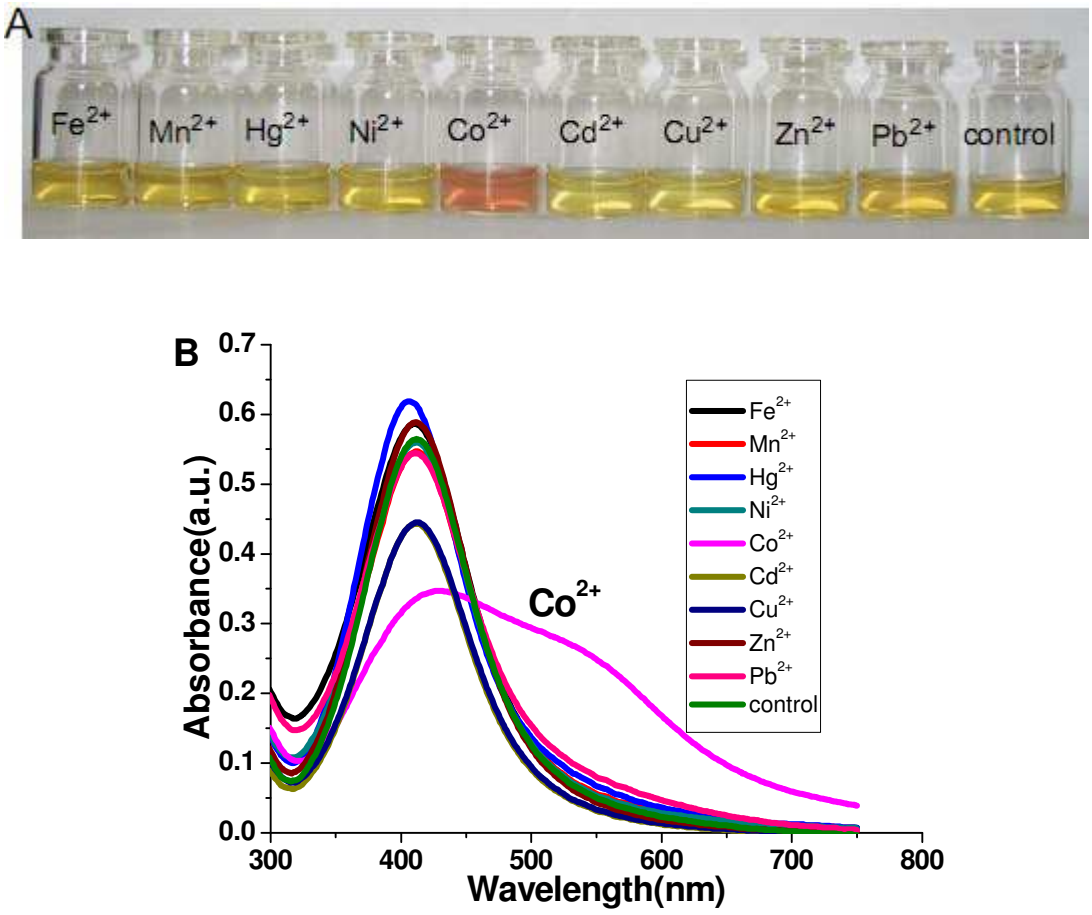


Figure.S4 The photographic images (A) and UV-*vis* absorption spectra (B) of triazole-carboxyl Ag NPs solution after adding transition metal ions (10 μM) for 5 mins. Typically, 0.5 mL of 50 μM various transition metal ions were added into 2 mL triazole-Ag NPs solutions and the combined solution mixed well for 5 mins and then tested.

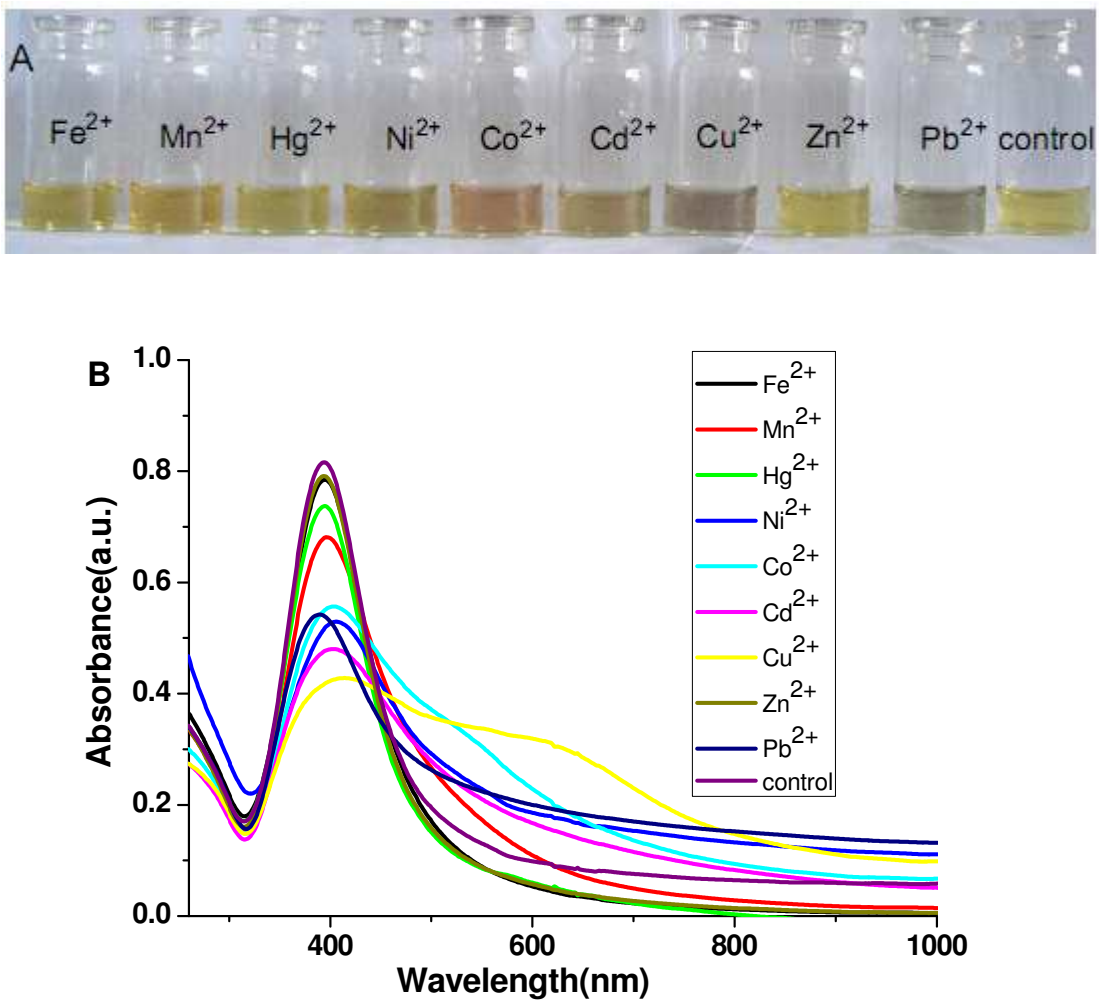


Figure S5 The photographic image (A) and UV-*vis* absorption spectra (B) of 2-mercaptoacetic acid modified Ag NPs (carboxyl-Ag NPs) solution after adding transition metal ions (50 μM) for 5 mins. Typically, 0.5 mL of 50μM various transition metal ions were added into 2 mL carboxyl-Ag NPs solutions and the combined solution mixed well for 5 mins and then tested.

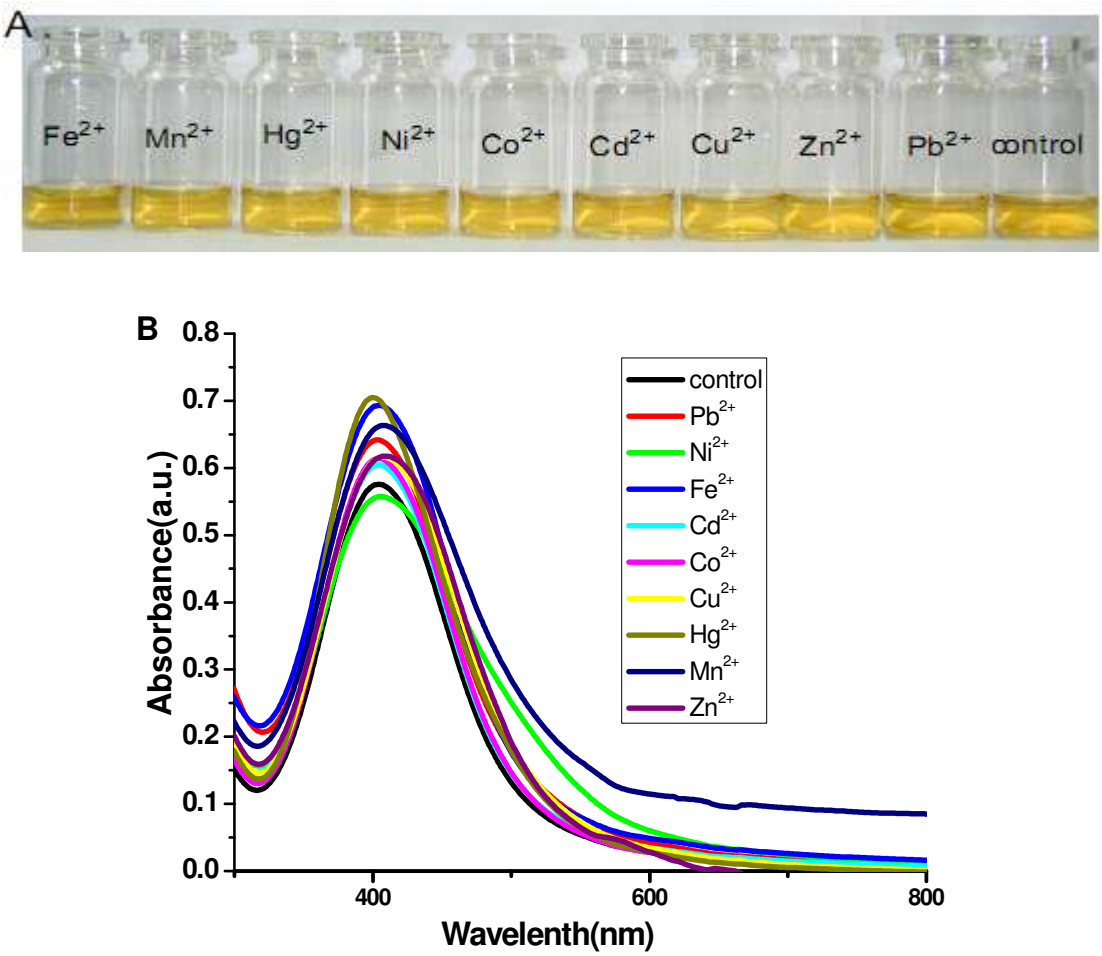


Figure. S6 The photographic images (A) and UV-*vis* absorption spectra (B) of triazole-Ag NPs solution after adding transition metal ions (10 μM) for 5 mins. Typically, 0.5 mL of 50 μM various transition metal ions were added into 2 mL triazole-Ag NPs solutions and the combined solution mixed well for 5 mins and then tested.

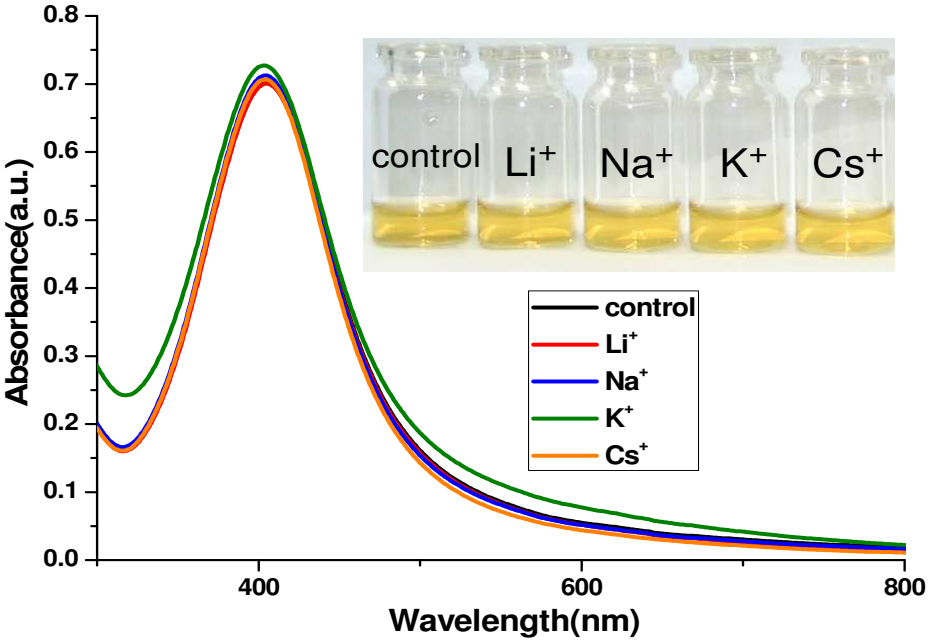


Figure.S7 The UV-*vis* absorption spectra and photographic images (inset) of triazole-carboxyl Ag NPs solution in the presence of 10 μM different metal ions. Typically, 0.5 mL of 50 μM various transition metal ions were added into 2 mL triazole-carboxyl Ag NPs solutions and the combined solution mixed well for 5 mins and then tested.

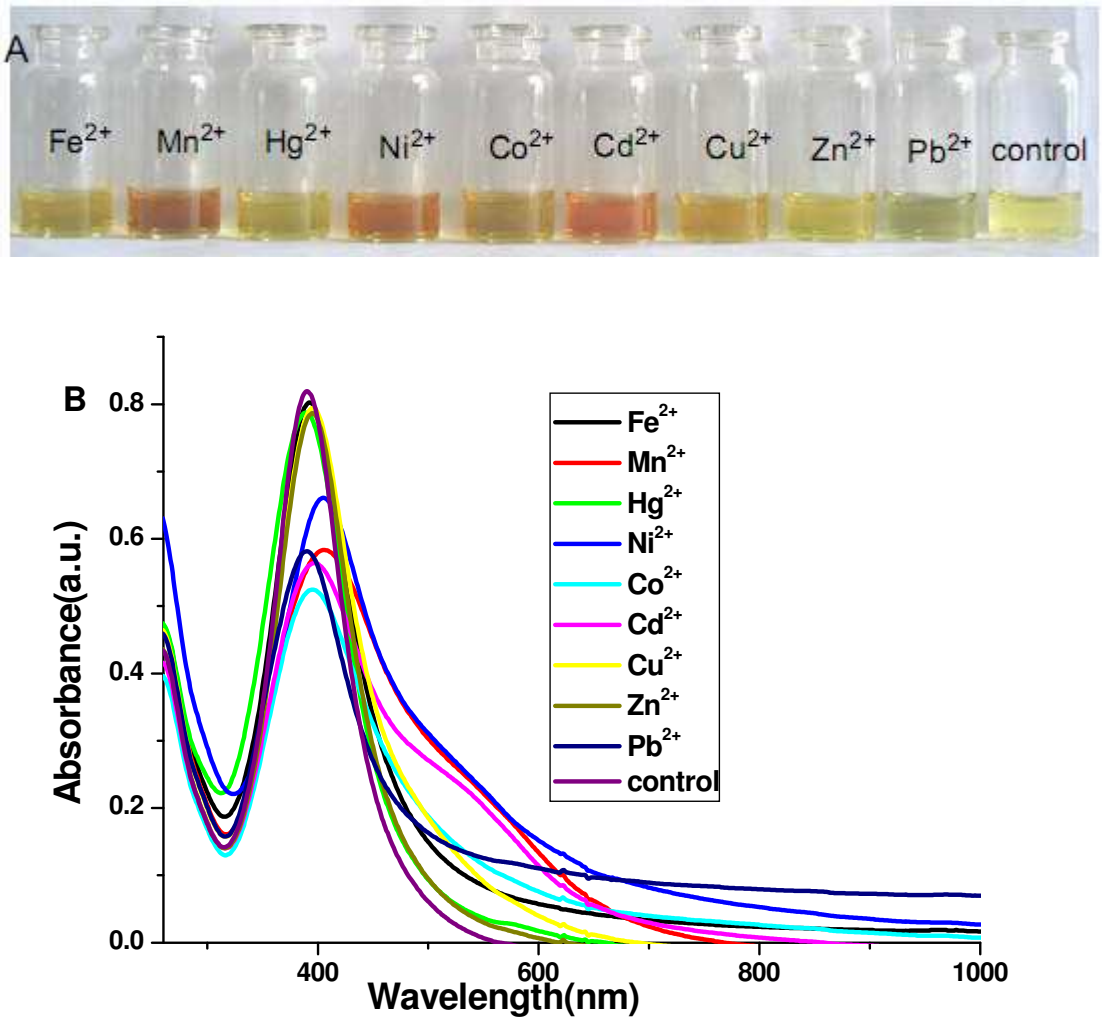


Figure. S8 The photographic image (A) and UV-*vis* absorption spectra (B) of alkynyl-carboxyl Ag NPs solution after adding transition metal ions (10 μM) for 5 mins. Typically, 0.5 mL of 50 μM various transition metal ions were added into 2 mL alkynyl-carboxyl Ag NPs solutions and the combined solution mixed well for 5 mins and then tested.

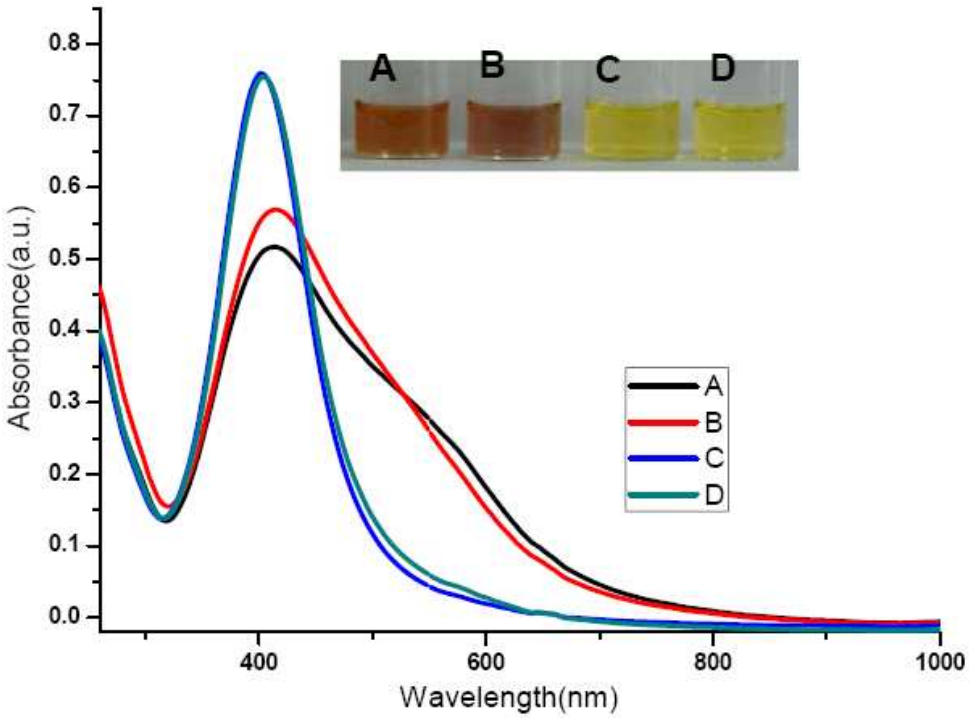


Figure. S9 Selectivity of the sensor for Co^{2+} in the mixture of metal ions (M): A) triazole-carboxyl Ag NPs + Co^{2+}; B) triazole-carboxyl Ag NPs + M + Co^{2+}; C) triazole-carboxyl Ag NPs + M; D) triazole-carboxyl Ag NPs + H_2O. M is the mixture of metal ions (Fe^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}). [Co^{2+}] = 10 μM, [Fe^{2+}] = [Mn^{2+}] = [Hg^{2+}] = [Ni^{2+}] = [Cd^{2+}] = [Cu^{2+}] = [Zn^{2+}] = [Pb^{2+}] = 50 μM.

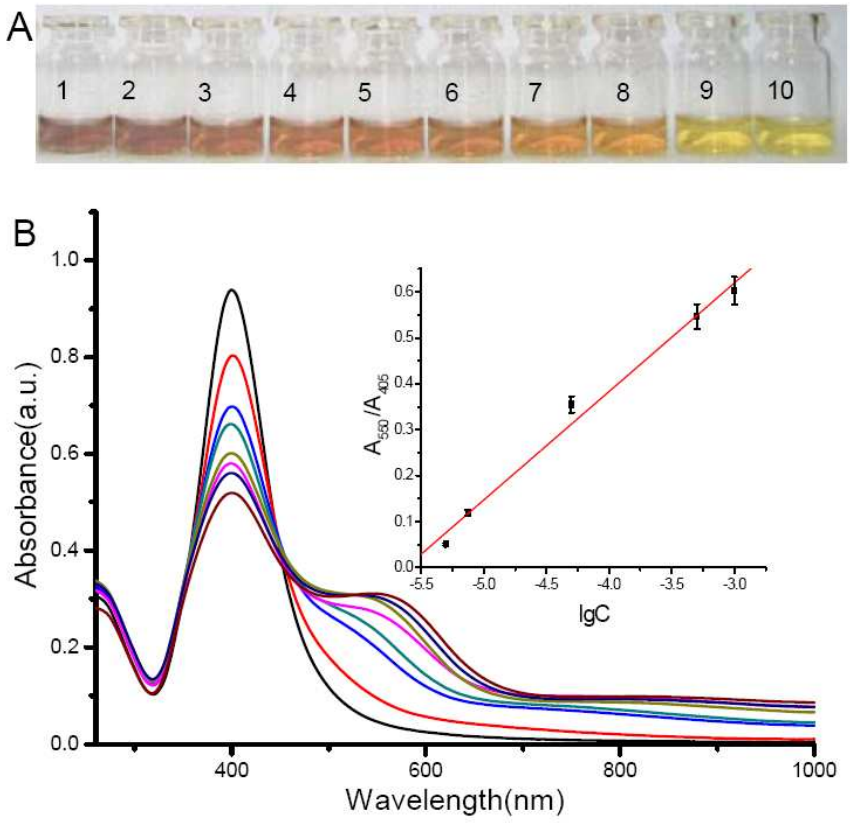


Figure. S10 (A) Photo images of triazole-carboxyl Ag NPs solution in the presence of other competitive ions (M) and various concentrations of Co^{2+} .The concentrations of Co^{2+} is: (1)7.5× 10^{-4} M; (2) 5.0× 10^{-4} M; (3) 2.5 × 10^{-4} M; (4) 1.0× 10^{-4} M; (5)7.5 × 10^{-5} M; (6) 5.0 × 10^{-5} M; (7)1.0 × 10^{-5} M; (8) 7..5 × 10^{-6} M; (9) 5.0 × 10^{-6} M; (10) 0 M.(B)The UV-*vis* adsorption spectra of the triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. Typically, 0.5 mL of various concentrations of Co^{2+} and 0.05 mM (M) were added into 2.0 mL triazole-carboxyl Ag NPs solutions, and the combined solution mixed well for 5mins and then tested. (M) is the mixture of metal ions solution, including 0.05 mM each of Fe^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}. The linear equation is $R = 1.32877 + (0.23638 \times \log [C])$ with a linearity coefficient of 0.99431. The colorimetric detection for Co^{2+} is 7.5 × 10^{-6} M.

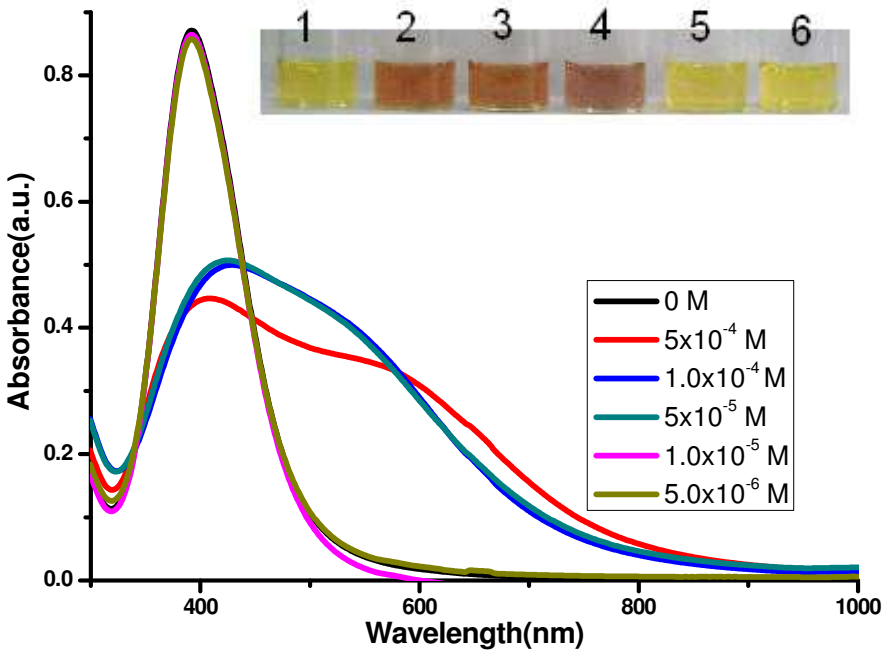


Figure. S11 Photo images and UV-*vis* adsorption spectra of f triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+} in drinking water. The concentrations of Co^{2+} in drinking water is: (1) 0 M; (2) 1.0×10^{-4} M; (3) 2.0×10^{-5} M; (4) 1.0×10^{-5} M; (5) 2.0×10^{-6} M; (6) 1.0×10^{-6} M. Typically, 0.5 mL of various concentrations of Co^{2+} in drinking water were added into 2.0 mL triazole-carboxyl Ag NPs solutions, and the combined solution mixed well for 5mins and then tested.