Supporting Information for

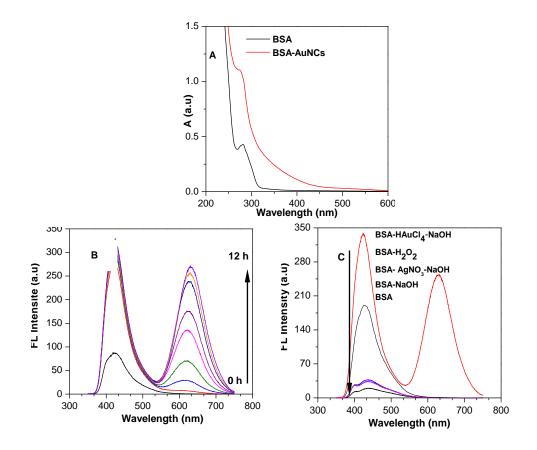
## Protein-gold Nanoclusters for Identification of Amino Acids by Metal Ions Modulated Ratiometric Fluorescence

Min Wang,<sup>1,2</sup> Qingsong Mei,<sup>1,2</sup> Kui Zhang<sup>1</sup> and Zhongping Zhang<sup>1,\*</sup>

<sup>1</sup>Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, Anhui, 230031, China.

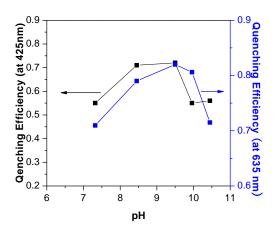
<sup>2</sup>Department of Chemistry, University of Science & Technology of China, Hefei, Anhui 230026, China

\*To whom correspondence should be addressed. *E-mail:* zpzhang@iim.ac.cn



**Fig. S1** (A) The UV-Vis absorption spectra of the aqueous solutions of BSA-AuNCs (red line) and BSA (black line) after the same reaction without HAuCl<sub>4</sub>. (B) Evolution of emission spectra with increasing the reaction time. The time is 0, 1.5, 3, 4.5, 6, 7.5, 9, 10.5, 12 h from the bottom to top. (C) Fluorescence spectra of control experiments.

During the synthesis, the color of solution changed from pale yellow to dark orange. At the first four hours, the emission of oxides of BSA formed and changed little in the next 8 hours (Fig.S1B). While the fluorescence of AuNCs formed gradually from 0 h to 12 h. To prove the origin of emission at 425 nm, the control experiments were also performed under the same condition as original experiment (Fig.S1C). Conditions of experiment were as following: the solution composed of BSA and NaOH; solution containing only BSA; solution containing AgNO<sub>3</sub>, BSA and NaOH; solution containing BSA and H<sub>2</sub>O<sub>2</sub>. The dual emissions form only in the presence of HAuCl<sub>4</sub>. If AgNO<sub>3</sub> substituted for HAuCl<sub>4</sub>, neither emission at 425 nm appeared which proved the origin of the fluorescence from oxides of BSA.



**Fig. S2** The relationship between FL quenching efficiencies of the emission at 425nm (black line) and at (blue line) and different pH values.

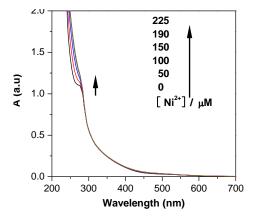
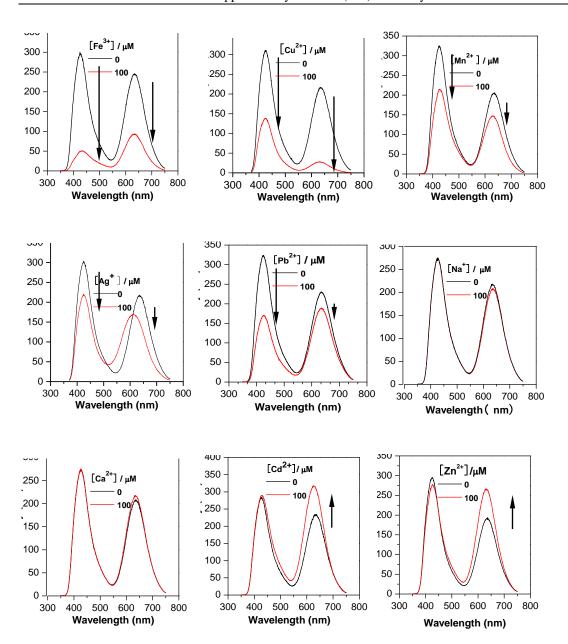


Fig. S3 The absorption spectra of BSA-AuNCs with additions of different amount of Ni<sup>2+</sup>.

Supplementary Material (ESI) for Analyst



**Fig. S4** The evolutions of florescence spectra of BSA-AuNCs in the presence of corresponding metal ions in solution at pH = 9.0.

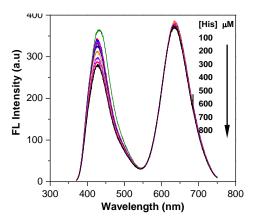


Fig. S5 Fluorescence spectra of BSA-AuNC in the presence of His without  $Ni^{2+}$  at pH = 9.5.

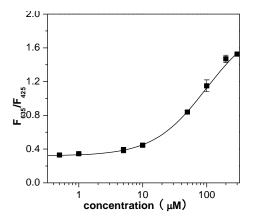


Fig. S6 The evolution of fluorescence ratio of BSA-AuNC upon the addition of different concentration of histidine in the presence of  $Ni^{2+}$ .

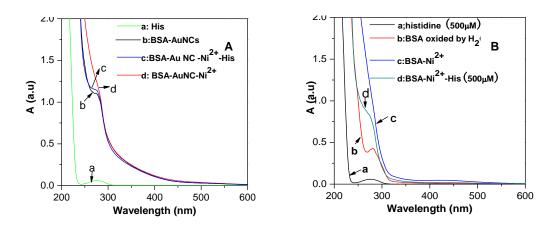
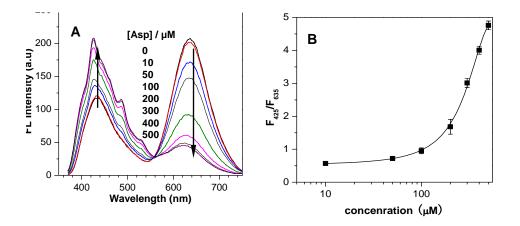
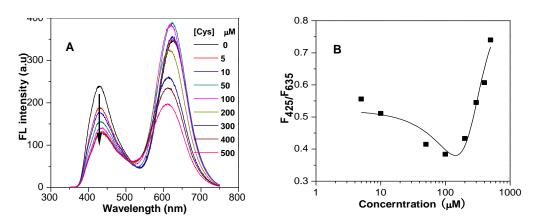


Fig. S7 The absorption spectra of BSA-AuNCs (A) and BSA oxided by  $H_2O_2$  (B) with the additions of Ni<sup>2+</sup>(225  $\mu$ M) and then His (500  $\mu$ M).

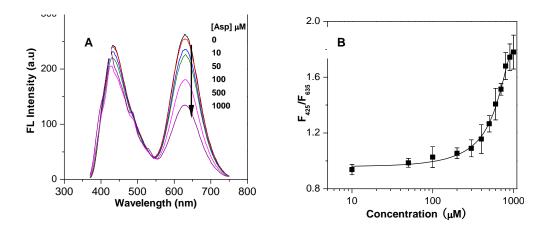


**Fig. S8** (A) Fluorescence spectra of BSA-AuNCs upon addition of different mounts of Asp in the presence of  $Pb^{2+}$  (225  $\mu$ M). (B) Evolution of fluorescence ratio of BSA-AuNC upon the addition of different concentrations of Asp at pH = 9.0 in the presence of  $Pb^{2+}$ .

Supplementary Material (ESI) for Analyst



**Fig. S9** (A) Fluorescence spectra of BSA-AuNCs upon addition of different mounts of Cys in the presence of  $Cd^{2+}$  (225  $\mu$ M). (B) Evolution of fluorescence ratio of BSA-AuNC upon the addition of different concentration of Cys at pH = 9.0 in the presence of  $Cd^{2+}$ .



**Fig. S10** (A) Fluorescence spectra of BSA-AuNCs upon addition of different mounts of Asp in the presence of  $Zn^{2+}$  (225  $\mu$ M). (B) Evolution of fluorescence ratio of BSA-AuNC upon the addition of different concentration of Asp at pH = 9.0 in the presence of  $Zn^{2+}$ .