

Supporting Information

Green emission and Ag⁺ sensing of hydroxy double salt supported gold nanoclusters

Jinyang Lu,^{a,b} Chunxiang Xu,^{*a} Zhengshan Tian,^a Junfeng Lu,^a Yi Lin^a and Zengliang Shi^a

^a State Key Laboratory of Bioelectronics, School of Biological Science & Medical Engineering, Southeast University, Nanjing 210096, China. *E-mail:* xcxseu@seu.edu.cn, *Tel:* 86-25-83790755

^b Department of Electronic Engineering, Suzhou Higher Vocational School of Technology, Suzhou 215009, China

The quantum yield of the AuNCs/Zn-HDS complex

The quantum yield of the complex is calculated according to the following equation:

$$QY_{sam} = QY_{ref} \frac{I_{sam} A_{ref} n_{sam}^2}{I_{ref} A_{sam} n_{ref}^2}$$

Where, “sam” and “ref” are referred to the AuNCs/Zn-HDS complex and quinine sulphate, respectively. “I” represents the integrated intensity of the emission peak. “A” is the absorption intensity, which is controlled below 0.05 to avoid reabsorption. “n” is the refractive index.

The absorption spectra of the complex and quinine sulphate in Fig. S1 show an intersection point at around 360 nm. In our measurement, 360 nm was selected as the excitation wavelength so that the $\frac{A_{ref}}{A_{sam}}$ term would be 1. Both the complex and quinine sulphate are dissolved in water, so that $\frac{n_{sam}}{n_{ref}} \approx 1$. According to the PL spectra with an excitation of 360 nm (Fig. S2), the quantum yield of the AuNCs/Zn-HDS complex is estimated as 7.6%, referring to 54% of quinine sulphate excited at the same wavelength.

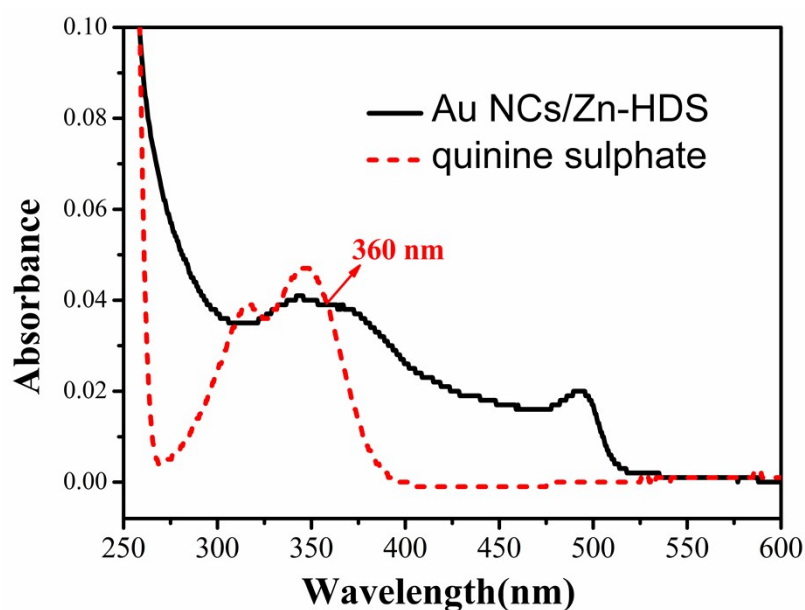


Fig. S1 The absorption spectra of the AuNCs/Zn-HDS complex and quinine sulphate.

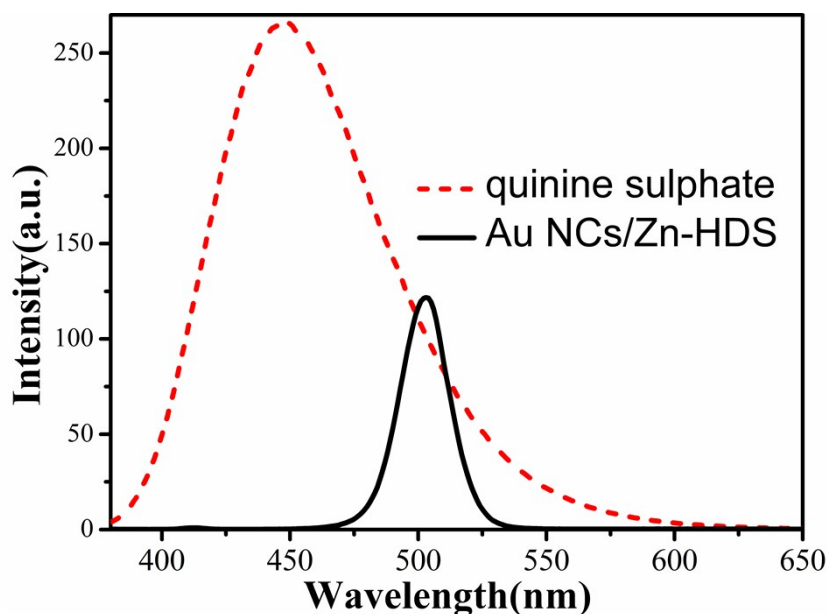


Fig. S2 The PL spectra of the AuNCs/Zn-HDS complex and quinine sulphate using 360 nm as the excitation wavelength.

The quenching mechanism of AuNCs/Zn-HDS complex for sensing Ag⁺

As mentioned in the main body of the manuscript, heavy metal ions like Pb²⁺, Hg²⁺ and Ag⁺ quenched 57%, 90% and 97% of the fluorescence. Coincidentally, Pb²⁺ (5d¹⁰), Hg²⁺ (5d¹⁰) and Ag⁺ (4d¹⁰) all possess d¹⁰ external electronic shell. In addition, the XPS spectrum of Au4f demonstrated the existence of Au⁺ (5d¹⁰) ions in the AuNCs/Zn-HDS complex. Thus, it is probable that the fluorescence quenching is caused by the formation of the strong d¹⁰-d¹⁰ metallophilic bonds. To verify this hypothesis, NaBH₄ (6 g/L), a strong reductant, was added into the Ag⁺-quenched solution. As shown in Fig. S3, the fluorescence intensity of the AuNCs/Zn-HDS complex increased firstly and then decreased until vanished. NaBH₄ can reduce Ag⁺ to Ag⁰, leading to the destruction of Au⁺-Ag⁺ bonds. Thus, the fluorescence was partially recovered. But excess NaBH₄ can reduce Au⁺ to Au⁰. As a result, the fluorescence was quenched again. This test supports our hypothesis.

Another possible mechanism is the coordination of Ag⁺ with carboxyl group. When KI (1.6 g/L) was added into the Ag⁺-quenched solution, the fluorescence would be recovered due to the insolubility of AgI. In fact, the fluorescence wasn't

recovered, as shown in Fig. S4. This experiment rules out the quenching mechanism due to the coordination of Ag^+ with the carboxyl group of 3MPA.

In conclusion, the quenching mechanism is attributed to the strong $d^{10}-d^{10}$ (Au^+-Ag^+) metallophilic bonds.

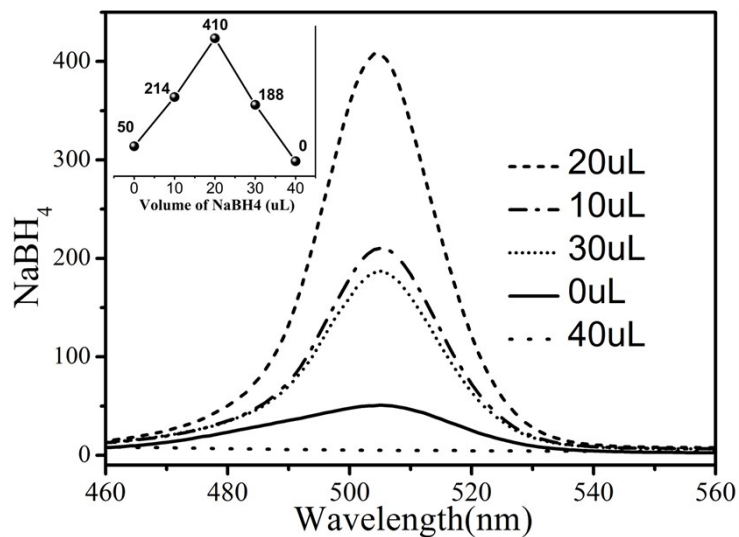


Fig. S3 The PL spectra of the AuNCs/Zn-HDS complex after adding different amount of NaBH_4 . The reaction time was 5 minutes.

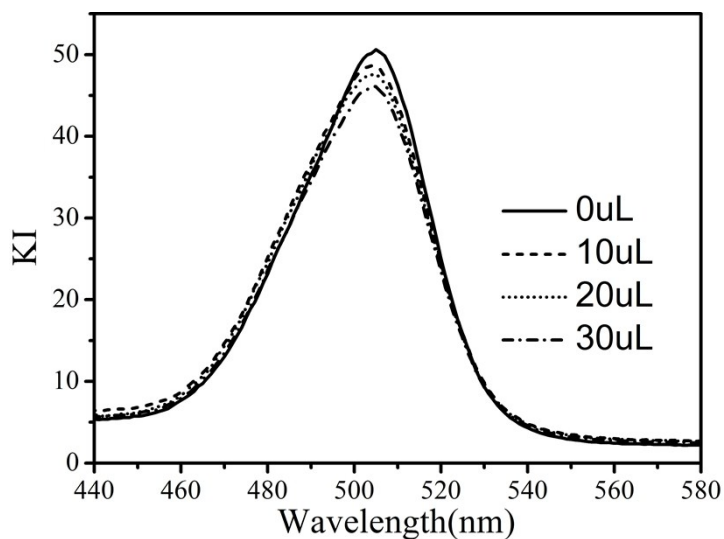


Fig. S4 The PL spectra of the AuNCs/Zn-HDS complex after adding different amount of KI. The reaction time was 5 minutes.