Supplementary Information

Gold Nanoparticle-based Colorimetric Probe for Rapid Detection of 1-Hydroxypyrene in Urine

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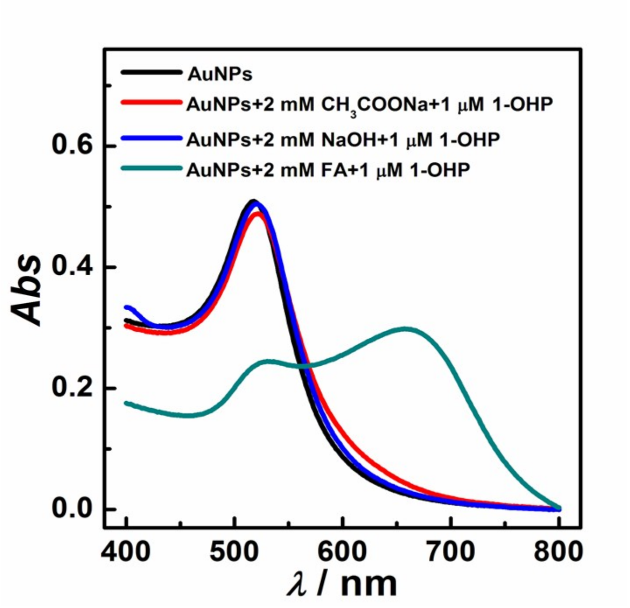


Fig. S1 UV/Vis absorption spectra responses of Au NPs, Au NPs with addition of 1 μM 1-OHP in the presence of 2 mM CH_3COONa, 2 mM NaOH and 2 mM FA.

Table S1. Effects of Different acids for Au NPs aggregations.

Acids	pKa[1]	A_{670}/A_{518}[a]	A_{670}/A_{518}[b]
None	—	0.028	—
Sulfuric acid	-3.00	0.54	—
FA	3.75	0.050	1.13
Propanoic acid	4.87	0.037	0.25

[1] pKa values are obtained from Lange's Handbook.

[a] Au NPs only with the addition of 2 mM acids, [b] Au NPs with the addition of 2 mM acids and 1 μM 1-OHP.—represents that data are not needed.

To further validate the specificity of the FA toward Au NPs aggregations, colorimetric responses of Au NPs with sodium acetate, sodium hydroxide, sulfuric acid, and propanoic acid instead of FA were investigated, respectively. If FA was changed to sodium acetate or sodium hydroxide, no aggregation was observed as shown in Fig. S1. If FA was changed to sulfuric acid, sulfuric acid could cause strong aggregation of Au NPs in the absence of 1-OHP due to carboxylic anions on the Au NPs surface obtaining enough H^+ to form abundant carboxylic acid, which led to complete destruction of electrostatic repulsion interaction between Au NPs (Table S1). However, for some weaker acid (such as FA and propanoic acid), aggregations of Au NPs were not observed. The addition of 1 μM 1-OHP cause different degree of aggregation of Au NPs. With a value of A_{670}/A_{518} value as a reference signal, FA showed a larger value. These results demonstrated that FA was critical to rapidly induce Au NPs aggregations when 1-OHP was subsequently added. Therefore, FA as an effective aggregation promoter was selected.

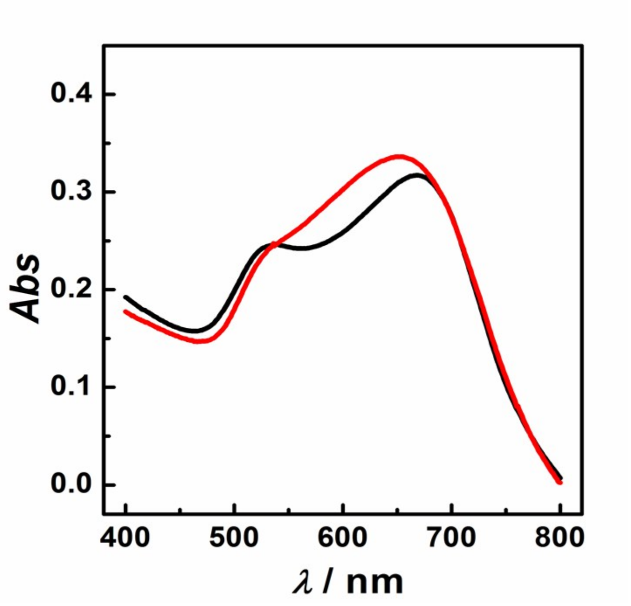


Fig. S2 UV/Vis absorption spectra responses of Au NPs (pH=6.2) with the addition of 1 μM 1-OHP in the presence of 2 mM FA (black curve), Au NPs (pH =6.2) adjusted by sulfuric acid with addition of 1 μM 1-OHP (red curve).

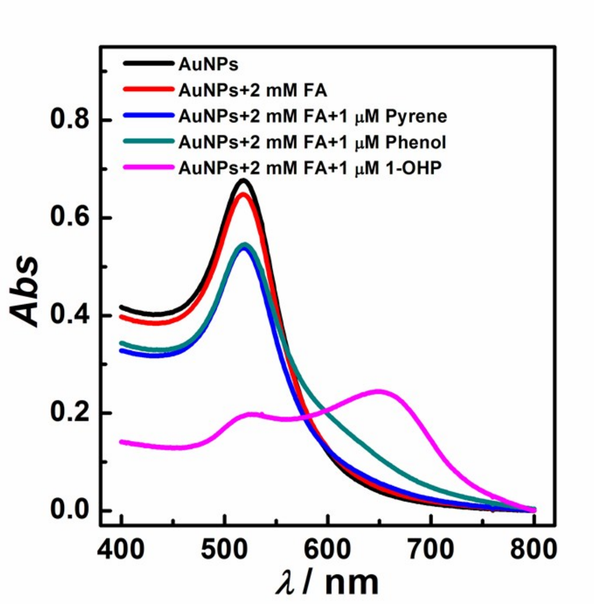


Fig. S3 UV/Vis absorption spectra responses of Au NPs, Au NPs with the addition of 2 mM FA, Au NPs with the addition of the 1 μM Pyrene, 1 μM Phenol and 1 μM 1-OHP in the presence of 2 mM FA.

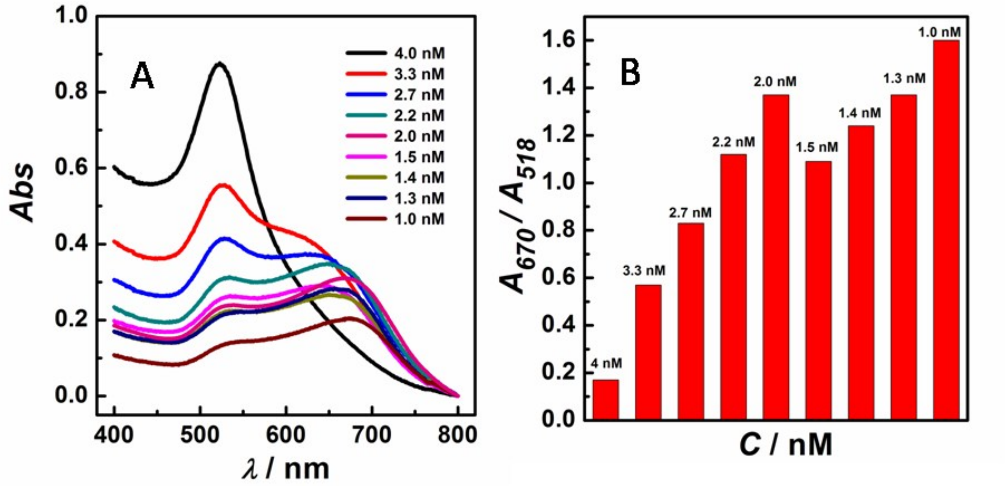


Fig. S4 (A) UV/Vis absorption spectra responses of Au NPs with different concentrations containing 1.0 nM, 1.3 nM, 1.4 nM, 1.5 nM, 2.0 nM, 2.2 nM, 2.7 nM, 3.3 nM, 4.0 nM with the addition of 2 mM FA and 1 μM 1-OHP. (B) The dependence of related absorbance ratio (A_{670}/A_{518}) on the Au NPs concentrations.

The concentration of as-prepared Au NPs suspension was 4.0 nM. As shown in Fig. S4A, upon decreasing the concentration of Au NPs from 4 nM to 2.0 nM, the absorption peak at 518 nm was gradually decreased, and a new absorption peak at 670 nm was appeared. Meanwhile, the value of A_{670}/A_{518} was gradually increased, and the larger value was appeared at 2 nM (Fig. S4B). Then the A_{670}/A_{518} value decreased a little at 1.5 nM, and gradually increased from 1.5 nM to 1.0 nM, the largest A_{670}/A_{518} value was obtained at 1.0 nM. Through the A_{670}/A_{518} value at 1.0 nM was larger than that of 2.0 nM, in consideration of Au NPs with low concentration had a light color and was unsuitable to carry out the naked-eye observation. Thus, we chose Au NPs with 2.0 nM to be the best concentration for the sensor system to ensure the best aggregation response and colorimetric observation.

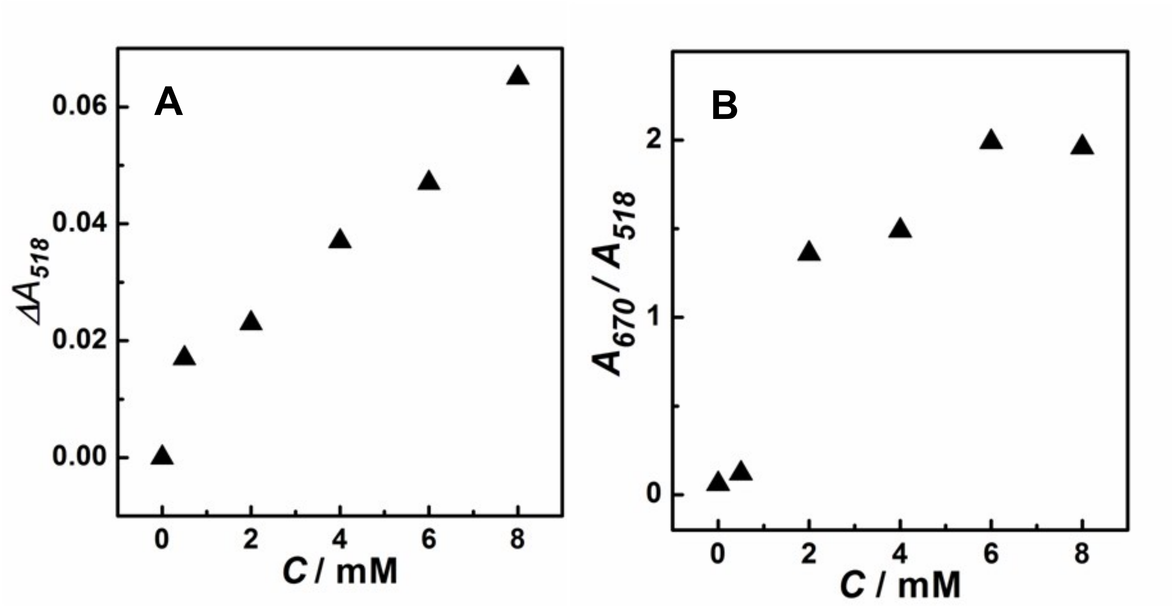
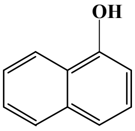
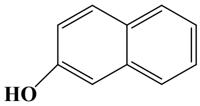
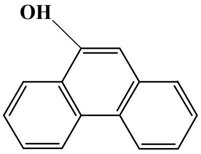
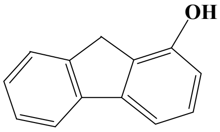
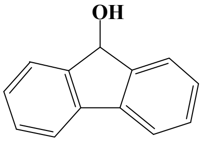
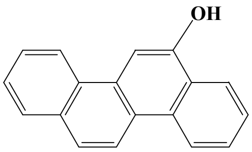
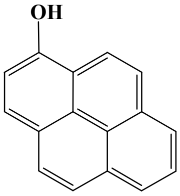


Fig. S5 (A) The dependence of related difference value of absorption at 518 nm ($\Delta A_{518}=A_0$-A) on the FA concentrations, A_0 and A represent absorption spectra of Au NPs without FA and Au NPs with different concentrations of FA containing 0 mM, 1.0 mM, 2.0 mM, 4.0 mM, 6.0 mM, and 8.0 mM. (B) The dependence of the related absorbance ratio (A_{670}/A_{518}) with the addition of 1 μM 1-OHP in the presence of the FA with different concentrations containing 0 mM, 1.0 mM, 2.0 mM, 4.0 mM, 6.0 mM, and 8.0 mM.

The effect of FA on the aggregation Au NPs was investigated as shown in Fig. S5. The proper FA concentration was selected based on: (1) FA could keep the stability of Au NPs, and decrease the background; (2) the addition of 1-OHP could induce the strong and rapid aggregations of Au NPs. The difference absorption at 518 nm ($\triangle A_{518}$) was applied for evaluated the effect of FA on the aggregation of Au NPs as shown in Fig. S5A. With the FA concentration increasing from 0 mM to 8.0 mM, the $\triangle A_{518}$ value gradually increased which demonstrated that the stability of Au NPs reduced. On the other hand, the effect of FA on the Au NPs aggregations in the presence of 1 μM 1-OHP was also investigated as shown in Fig. S5B. It was found that the colorimetric response (A_{670}/A_{518}) was slightly increased at 0.5 mM compared with that at 0 mM, and obtained a higher response at 2 mM FA. The gradually increased response was also observed with FA concentration range from 4 mM to 8 mM. It was found that the A_{670}/A_{518} value was 91%

and 69% of that at 4 mM and 6 mM. In view of the stability of Au NPs (smaller △A_{518} value) and larger aggregation response with the addition of 1-OHP (larger A_{670}/A_{518} value), we chose 2 mM FA was selected for sensing 1-OHP.

Table S2. Relevant material molecular structures used in this work

	Abbreviation	Structure
1-hydroxynaphthalene	1-OHN	
2-hydroxynaphthalene	2-OHN	
9-hydroxyphenanthrene	9-OHP	
2-hydroxyfluorene	2-OHF	
9-hydroxyfluorene	9-OHF	
6-hydroxychrysene	6-OHC	
1-hydroxypyrene	1-OHP	

References

1. J. A. Dean. Lange's Handbook of Chemistry 13th Edition, Knoxville, USA, 1991, Chapter 5, page 11-62.