Electronic Supplementary Information

Exploring and Exploiting the Synergy of Non-Covalent Interactions on the Surface of Gold Nanoparticles for Fluorescent Turn-On Sensing of Bacterial Lipopolysaccharide

Jinhong Gao, Yangwei Lai, Chuanliu Wu*, and Yibing Zhao*

Department of Chemistry, College of Chemistry and Chemical Engineering and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen, 361005, P. R. China.

*To whom correspondence should be addressed, Email: chlwu@xmu.edu.cn, ybzhao@xmu.edu.cn.

Table of content

1. Figure S1 shows the TEM images and absorption spectra of Au NPs
2. Figure S2 shows the hydrodynamic size and Zeta potential of Au NPs
3. Figure S3 shows the $^1$H-NMR of 2-4
4. Introduction of Hill equation
5. Figure S4 shows the fluorescence spectra of 3 upon gradual addition of MTA-Au
6. Figure S5 shows the time-dependent fluorescence quenching of 4 by MTA-Au
7. Figure S6 shows the fluorescence quenching of 1-4 in the present of MUA-Au
8. Figure S7 shows the Hill plots of the fluorescence quenching of 1-4 by MUA-Au
9. Figure S8 shows the kinetics of fluorescence recovery of 2-4 upon addition of LPS
10. Figure S9 shows the effect of LPS on the fluorescence of 2-4
Figure S1. TEM images of sodium citrate coated Au NPs, citrate-Au (a), MTA-Au (b), and MUA-Au (c); UV-Vis absorption spectra of various Au NPs (d).
Figure S2. Hydrodynamic size of citrate-Au, MUA-Au and MTA-Au measured by DLS (top); Zeta-potential (bottom) of citrate-Au in water and that of MUA-Au and MTA-Au in 10 mM HEPES buffer (pH 7.0).
Figure S3. $^1$H NMR Characterization of fluorescent probes (2-4); up: $^1$H-NMR of 2; middle: $^1$H-NMR of 3; bottom: $^1$H-NMR of 4. The peaks in 4.5 ppm, 3.5 ppm, and 1 ppm are from ethanol residual, and the peak in 3.4 ppm and 2.5 ppm is from DMSO and H$_2$O, respectively.
Hill equation

The quenching of fluorescence can be quantified by:

\[ Q = \frac{F_0 - F}{F_0} \]  

(1)

where \( F_0 \) and \( F \) are fluorescence intensities of fluorescence probes 1-4 in the absence and presence of Au NPs, respectively.

The saturation value of \( Q \) can be defined as that \( Q_{\text{max}} \):

\[ Q_{\text{max}} = \frac{F_0 - F_\infty}{F_0} \]  

(2)

where \( F_\infty \) is the fluorescence intensity of 1-4 on the surface of Au NPs. Considering the super-high quenching efficiency of Au NPs to fluorescent probes (i.e., the fluorescence of the probes can be completely quenched upon binding on the surface of Au NPs), the value of \( F_\infty \) is set to 0. Thus, the \( Q_{\text{max}} \) can be assigned to 1.

We assume that the binding of fluorescent probes (1-4) to Au NPs occurs at equilibrium, and the fluorescence quenching data can be fitted by Hill equation with the introduction of \( K_d \) and \( n \) which describes the binding constant of 1-4 to Au NPs and the Hill coefficient, respectively. The Hill equation can be described as the following:

\[ \frac{Q}{Q_{\text{max}}} = \frac{[\text{Au}]^n}{[K_d^2+\text{[Au]}^n]} \]  

(3)

where \([\text{Au}]\) is the concentration of Au NPs.

By combining eq1, eq2, and eq3, the Hill equation can then be obtained as:

\[ \ln \frac{F_0 - F}{F} = n \cdot \ln[\text{Au}] - n \cdot \ln K_d \]  

(4)

This equation describes the quantitative relationship between fluorescence intensity of 1-4 and the concentration of Au NPs. By fitting the fluorescence quenching data with eq4, the binding constant \( K_d \) and Hill coefficient \( n \) of the binding of 1-4 to Au NPs can then be obtained.
**Figure S4.** Fluorescence titration spectra of 3 in HEPES buffer solution upon the gradual addition of MTA-Au with the concentration ranging from 0 to 0.158 nM; the excitation wavelength is 490 nm. Fluorescence titration spectra of 2 and 4 were not given.
Figure S5. Time dependent quenching of the fluorescence of 4 (50 nM) in HEPES buffer (10mM, pH 7.0, 20% ethanol) upon the addition of MTA-Au.
Figure S6. Fluorescence response of fluorescent probes (1-4, 50 nM) in the present of MUA-Au in HEPES buffer (10mM, pH 7.0, 20% ethanol); mean ± SD (n=3).

Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2013
Figure S7. Fluorescence quenching data of 1-4 by MUA-Au fitted with Hill equation (solid line).

The Hill coefficients obtained from the fluorescence quenching of 1-4 by MUA-Au are 0.79, 1.11, 0.84, and 0.62, respectively.
Figure S8. The kinetics of fluorescence turn-on of 2-MTA-Au, 3-MTA-Au, and 4-MTA-Au system in the presence of LPS (50 nM) in HEPES buffer (10mM, pH 7.0, 20% ethanol); mean ± SD (n=3).
**Figure S9.** The effect of LPS on the fluorescence of 2-4 in HEPES buffer (10mM, pH 7.0, 20% ethanol); concentration of 2-4: 50 nM; concentration of LPS ranging from 0 to 1 μM; data are presented as mean ± SD (n=3). It should be noted that the presence of LPS influences, to some extent, the fluorescence intensity of 2-4, the effect which is, however, negligible as compared to the effect of Au NPs. Thus, the observed fluorescent recovery for the 2/3/4-MTA-Au systems upon the addition of LPS was largely resulted from the dissociation of fluorescence probes from the surface of Au NRs.