Supporting Information

A colorimetric selective sensing probe for calcium ions with tunable dynamic ranges using cytidine triphosphate stabilized gold nanoparticles

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Chemicals and Apparatus: All chemicals used were of analytical grade or of the highest purity available. Chloroauric acid (HAuCl₄·3H₂O), citric acid, buffers, and metal salts were purchased from Sigma Aldrich (USA). All glassware was cleaned thoroughly with freshly prepared aqua regia (3:1 (v/v) HCl/HNO₃) and rinsed thoroughly with Milli-Q water prior to use. Milli-Q water was used to prepare all the solutions in this study. UV/Vis spectrometry was carried out with S-3100 purchased from SCINCO. TEM images of AuNPs were captured on a JEM-2100 purchased from JEOL (operating at 200 kV). Samples for TEM measurements were prepared by placing 30 μL of the AuNPs solution on a carbon-coated copper grid and then drying at room temperature.

Preparation of CTP-AuNPs: The CTP-AuNPs were prepared based upon a reported method. All glassware was washed with freshly prepared aqua regia (3:1=HCl:HNO₃) followed by extensive rinsing with doubly distilled H₂O. Citric acid stabilized Au particles with a diameter of 13 nm were prepared by adding 50 mL of a citrate solution (38.8 mM) to 500 mL of boiling 1.0 mM HAuCl₄·3H₂O with vigorous stirring. After the appearance of deep red color, boiling and stirring were continued for 15 min. The solution was then allowed to cool to room temperature with continued stirring. The citric acid stabilized AuNPs were mixed with the CTP solution and the solution was incubated for 5 minutes. The solution concentration was adjusted using 10 mM sodium phosphate buffer (pH 7.0, 0.025 M NaCl) so that the final concentrations of AuNPs and CTP were 3 nM and 0.3 mM, respectively.
Colorimetric assay for Ca$^{2+}$

Solutions of AuNPs (3 nM) in SPB buffer (pH 7.0, 0.025 M NaCl, 0.3 mM CTP) were mixed with various concentrations of Ca$^{2+}$ and the UV/Vis spectra of the solutions were recorded after incubation for 5 minutes.

Determination of selectivity

Solutions of AuNPs (3 nM) in SPB buffer (pH 7.0, 0.025 M NaCl, 0.3 mM CTP) were mixed with various metal ions, such that the final concentration was 0.6 mM. The UV/Vis spectra of the solutions were recorded after incubation for 5 minutes.

pH dependence of sensing

Aqueous buffer solutions (pH 4.0-9.0) containing AuNPs (3 nM) and CTP (0.3 mM) with Ca$^{2+}$ (0.6 mM) were prepared, and their UV–visible absorbances at 600 nm were measured after incubation for 5 min. The compositions of the buffer solutions are as follows: pH 4.0 (acetate buffer 10 mM, NaCl 0.025 M), pH 5.0 (acetate buffer 10 mM, NaCl 0.025 M), pH 6.0 (acetate buffer 10 mM, NaCl 0.025 M), pH 7.0 (sodium phosphate buffer 10 mM, NaCl 0.025 M), pH 8.0 (tris buffer 10 mM, 0.025 M), and pH 9.0 (tris buffer 10 mM, 0.025 M).

The absorbance spectra of CTP-AuNPs in the presence of Ca$^{2+}$ (0.6 mM) and followed by addition of EDTA (6 mM).
The detection limit of the CTP-AuNPs with Ca$^{2+}$

\[ y = 1.55662x + 5.51921 \]

LOD = 0.28mM

The absorbance spectra of CMP-AuNPs and CDP-AuNPs in the presence of various metal ions

**CMP-stabilized AuNPs**

※ UV/Vis spectra obtained 5 min after addition of various cations (0.6 mM) to pH 7.0 buffer solution (10 mM sodium phosphate buffer (SPB) + 0.025 M NaCl) containing CMP-stabilized AuNPs (3 nM)
UV/Vis spectra obtained 5 min after addition of various cations (0.6 mM) to pH 7.0 buffer solution (10 mM sodium phosphate buffer (SPB) + 0.025 M NaCl) containing CDP-stabilized AuNPs (3 nM)