Electronic Supplementary Information

Colorimetric assay for cyanide and cyanogenic glycoside using polysorbate 40-stabilized gold nanoparticles

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EXPERIMENTAL SECTION

Chemicals. Trisodium citrate, ethylenediaminetetraacetic acid (EDTA), PS 40, taurine, linamarin, NaOH, H_2SO_4, and NaCN were ordered from Sigma-Aldrich (Louis, MO). Hydrogen tetrachloroaurate (III) dehydrate were purchased from Alfa Aesar (Ward Hill, Ma). $NaHPO_4$, and NaCl were ordered from J.T. Baker (Philipsburg, NJ). LiCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $Cd(ClO_4)_2$, $AlCl_3$, $Pb(NO_3)_2$, and $HgCl_2$, were purchased from Acros (Geel, Belgium). CH_3COONa, NaBr, $NaBrO_3$, $NaClO_4$, Na_2CO_3, $NaHCO_3$, NaF, KIO_3, NaI, $NaNO_2$, $NaNO_3$, Na_3PO_4, Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$, KSCN, and Na_3BO_3 were obtained from Merck (Darmstadt, Germany). H_3PO_4 was bought from RdH (Buchs, Switzerland). Water used in all experiments was doubly distilled and purified by a Milli-Q system (Millipore, Milford, MA).

Nanoparticle Synthesis. Citrate-capped AuNPs are prepared by reducing metal salt precursor (hydrogen tetrachloroaurate, $HAuCl_4$) in a liquid phase. Briefly, 10 mL of 38.8 mM trisodium citrate was added rapidly to 100 mL of 1 mM $HAuCl_4$ that was heated under reflux. Heating under reflux was continued for an additional 15 min, during which time the color changed to deep red. The images of transmission electron microscopy (TEM) (H7100, Hitachi High-Technologies Corp., Tokyo, Japan) confirmed that the size of citrate-AuNPs is 13 ± 1 nm. The extinction spectra of citrate-AuNPs were recorded using a UV-visible spectrophotometer (V-530, Jasco, Hachioji, Japan). The surface plasmon resonance (SPR) peak of 13 nm AuNPs was 520 nm, indicating that their extinction coefficient is 2.78×10^8 M^{-1} cm^{-1}. The particle concentration of the as-prepared AuNPs was estimated to be 15 nM using Beer's law. The PS 40-AuNPs were obtained when 100 μL of 100% PS 40 was added to a solution of 15 nM citrate-capped AuNPs (10 mL).[1] The resulting mixture was

stored at 4°C until further use.

Nanoparticle Characterization. To understand the sensing mechanism, we equilibrated aliquots (500 μL) of 1 nM PS 40-AuNPs in the absence and presence of 5 μM cyanide for 30 min at ambient temperature. The resulting solutions were subjected to centrifugation at 17 000 rpm for 20 min. After removal of the supernatants, the precipitates were washed with water. After two centrifugation/washing cycles, the pellets were resuspended in water. A portion of the sample (1 μL) was s pipetted into a stainless steel 384-well target (Bruker Daltonics) and dried under ambient temperature. Surface-assisted laser desorption/ionization time-of-flight mass spectrometry (SALDI-TOF MS) (Autoflex, Bruker) was conducted using a 337-nm-diameter nitrogen laser with a 3 ns pulse width.

For inductively-coupled plasma MS (ICP-MS) (Perkin-Elmer-SCIEX, Thornhill, ON, Canada) measurements, a solution containing 1 nM PS 40-AuNPs, 5x PBS, and 0–100 μM cyanide was centrifuged at 17 000 rpm for 20 min. The obtained supernatants were diluted to 100-fold and then measured by ICP-MS.

Sample preparation. We prepared 1x phosphate-buffered saline (1x PBS; pH 7.4) by dissolving Na_2HPO_4 (22.05 g), NaH_2PO_4 (2.07 g), and NaCl (4.5 g) in H_2O (1.0 L). Stock solutions of metal ions and anions were dissolved in deionized water while PS 40-AuNPs were prepared in 5x PBS at pH 7.4. Cyanide (500 μL, 5 μM), metal ions (500 μL, 500 μM), or anions (500 μL, 500 μM) were added to solutions of PS 40-AuNPs (500 μL, 1 nM). We equilibrated the resulting solutions at ambient temperature for 30 min and then recorded the extinction spectra of the solutions. For sensing linamarin, linamarin was first dissolved in a solution containing H_3PO_4 (1 mL, 0.1 M) and H_2SO_4 (9 mL, 5 M).[2] A solution containing linamarin (10–150 μM) was refluxed in a boiling water bath for 3 h and then cooled in ice water. The resulting solution (1 mL) was neutralized with NaOH (4 mL, 2.5 M). Hydrolyzed linamarin

(500 μL) was added to a solution of PS 40-AuNPs (500 μL, 2 nM). We equilibrated the resulting solutions at ambient temperature for 30 min, and then collected their extinction spectra.

Analysis of Real Samples. Samples of drinking and tap water were collected from National Sun Yat-sen University campus. We then prepared a series of samples by "spiking" them with standard solutions of cyanide (0–6 μM). These spiked samples (500 μL) were added to a solution of 5x PBS containing PS 40-AuNPs (500 μL, 1 nM). We incubated the resulting solutions for 30 min before measuring their extinction spectra. This method was also utilized to detect linamarin in cassava root. Fresh cassava root was bought at local market. Samples of cassava root (2 g) were cut into small cubes and then ground with a zest grater. To monitor the removal of cyanide during food processing, the obtained powders were prepared in deionized water (5 mL) and then heated to 65 °C for 0–120 min. A portion of the resulting solution (500 μL) was detected using a solution of 5x PBS containing PS 40-AuNPs (500 μL, 1 nM). Moreover, these powders were spiked with standard solutions of linamarin (5 mL, 0–500 μM) and then stored in sealed tubes for 1 h at room temperature. After centrifugation, hydrolyzed linamarin-containing supernatants were diluted to 200-fold with deionized water. The diluted supernatants were detected by our proposed probe.

References

(1) (a) Lin, C. Y.; Yu, C. J.; Lin, Y. H.; Tseng, W. L. *Anal. Chem.* **2010,** *82,* 6830-6837.
(b) Huang, C. C.; Tseng, W. L. *Anal. Chem.* **2008,** *80,* 6345-6350.

(2) Bradbury, J. H.; Egan, S. V.; Lynch, M. J. *J. Sci. Food Agric.* **1991,** *55,* 277-290

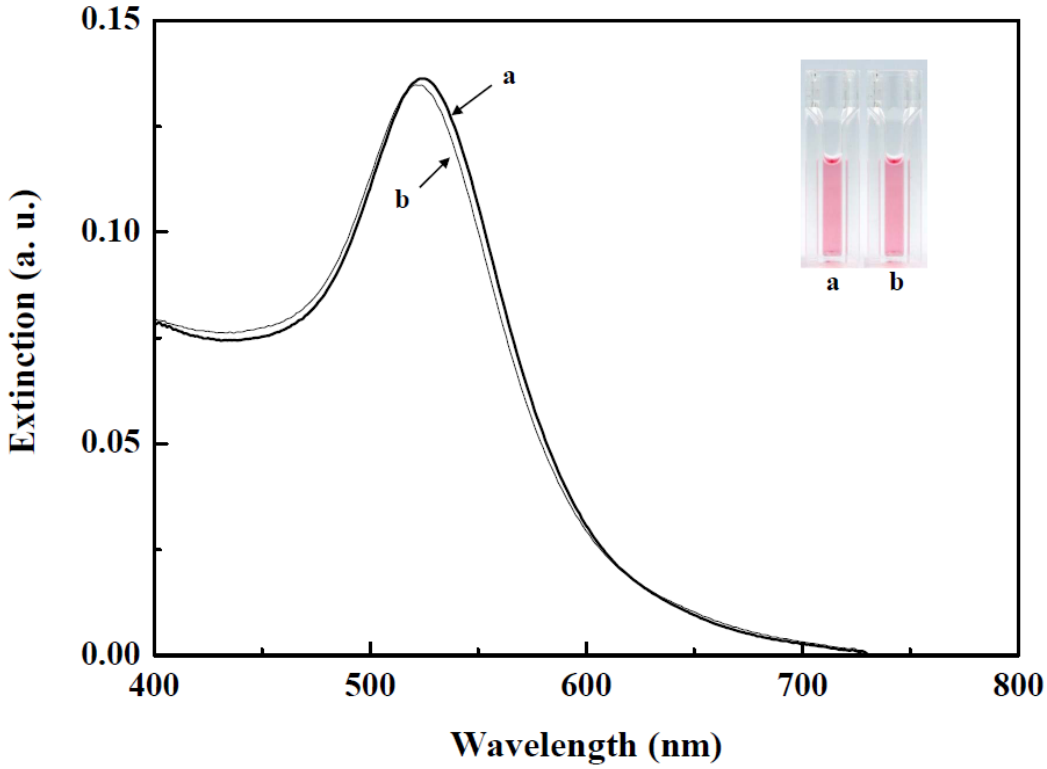

Figure S1. Extinction spectra and photo images of solutions of 1 nM PS 40-AuNPs (a) before and (b) after the addition of 5 μM cyanide. PS 40-AuNPs were prepared in deionized water. Cyanide was incubated with PS 40-AuNPs for 30 min.

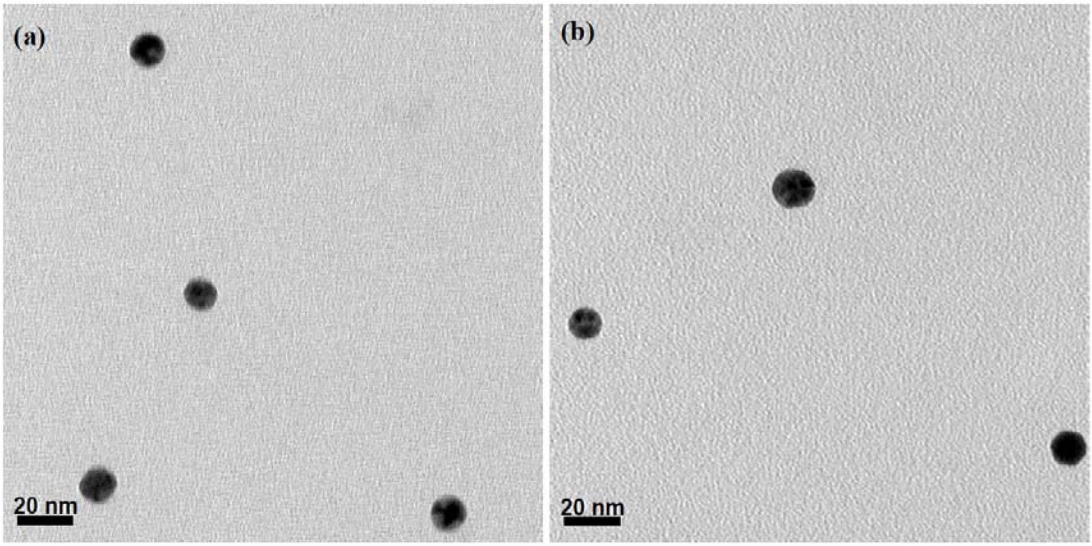

Figure S2. TEM images of solutions of 1 nM PS 40-AuNPs (a) before and (b) after the addition of 5 μM cyanide. PS 40-AuNPs were prepared in deionized water. The incubation time is 30 min. The scale bar is 20 nm.

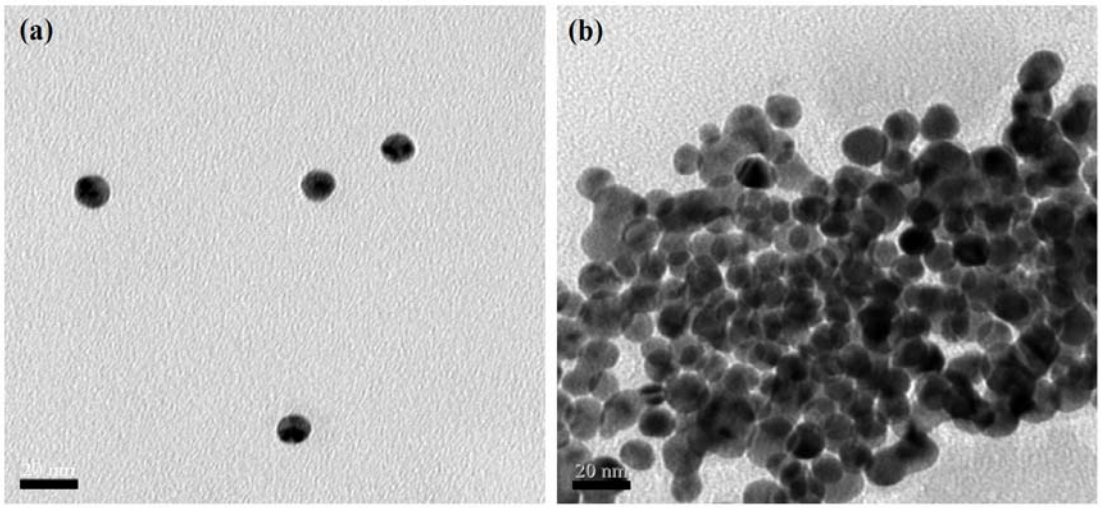

Figure S3. TEM images of solutions of 1 nM PS 40-AuNPs (a) before and (b) after the addition of 5 μM cyanide. PS 40-AuNPs were prepared in 5x PBS. The incubation time is 30 min. The scale bar is 20 nm.

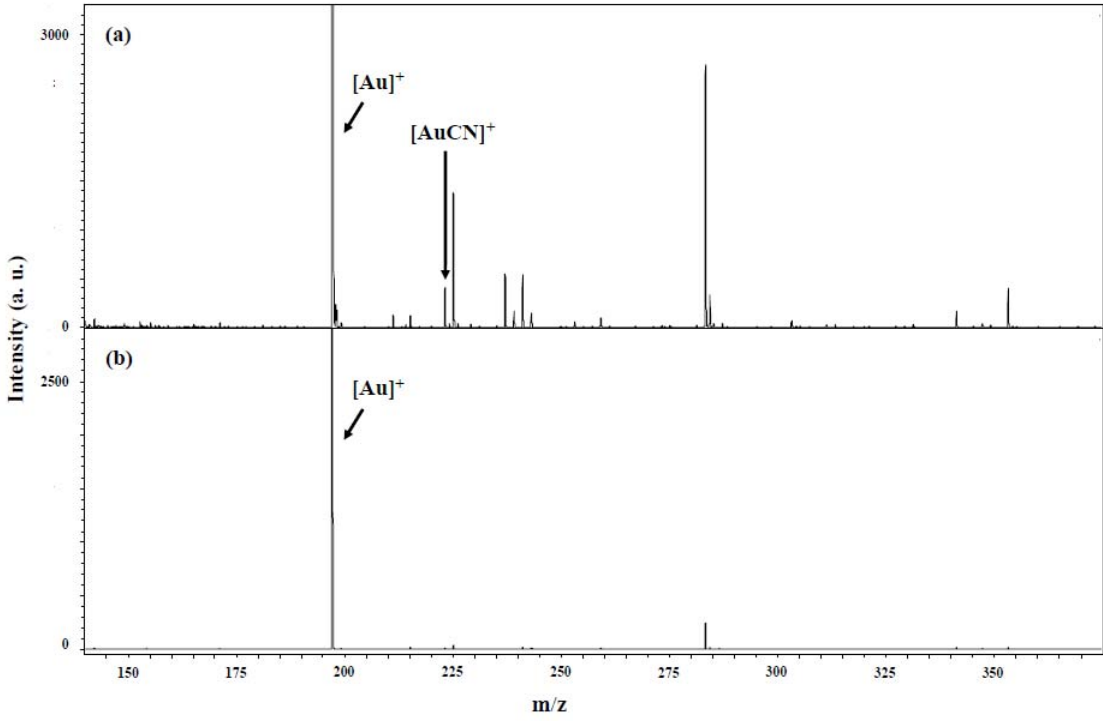

Figure S4. SALDI spectra of the precipitated AuNPs obtained from a 5x PBS solution containing (a) 1 nM PS 40-AuNPs and 5 μM cyanide and (b) 1 nM PS 40-AuNPs. The precipitates were washed by two centrifugation/re-dispersion cycles.

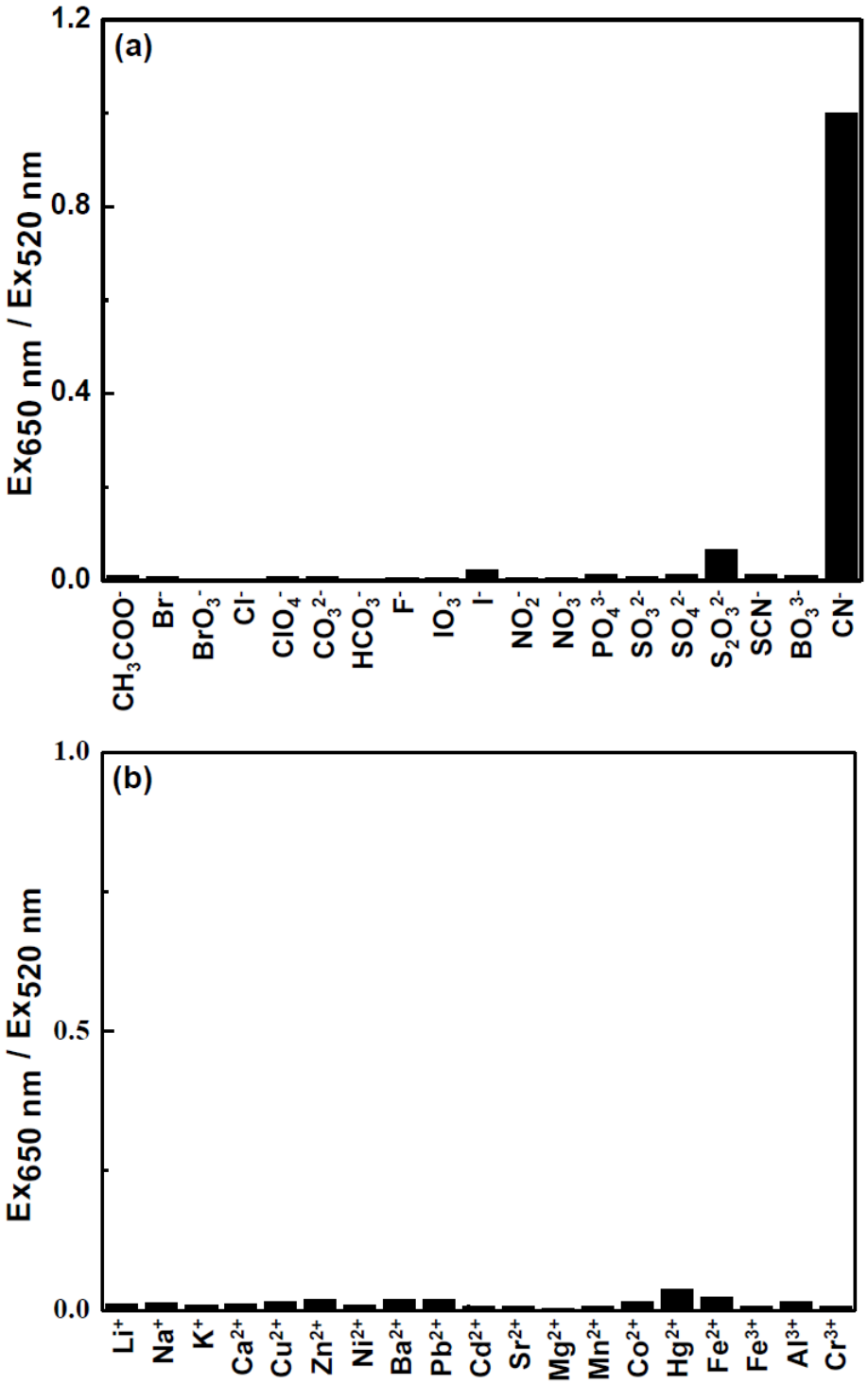

Figure S5. The value of $Ex_{650\ nm}/Ex_{520\ nm}$ of a solution containing 1 nM PS 40-AuNPs and 5x PBS upon the addition of (a) 5 μM cyanide and 500 μM anions and (b) 500 μM metal ions. The incubation time is 30 min.

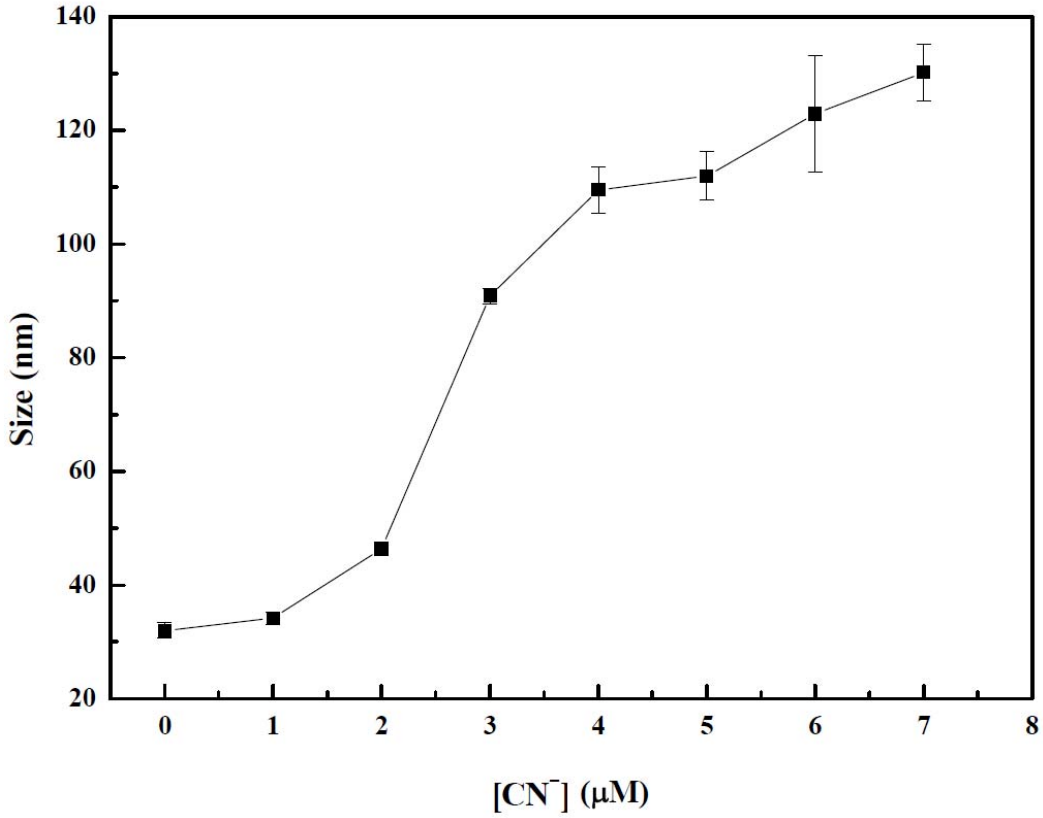

Figure S6. Hydrodynamic size of solutions of 1 nM PS 40-AuNPs upon the addition of 0–7 μM cyanide. PS 40-AuNPs were prepared in 5x PBS. The incubation time is 30 min.

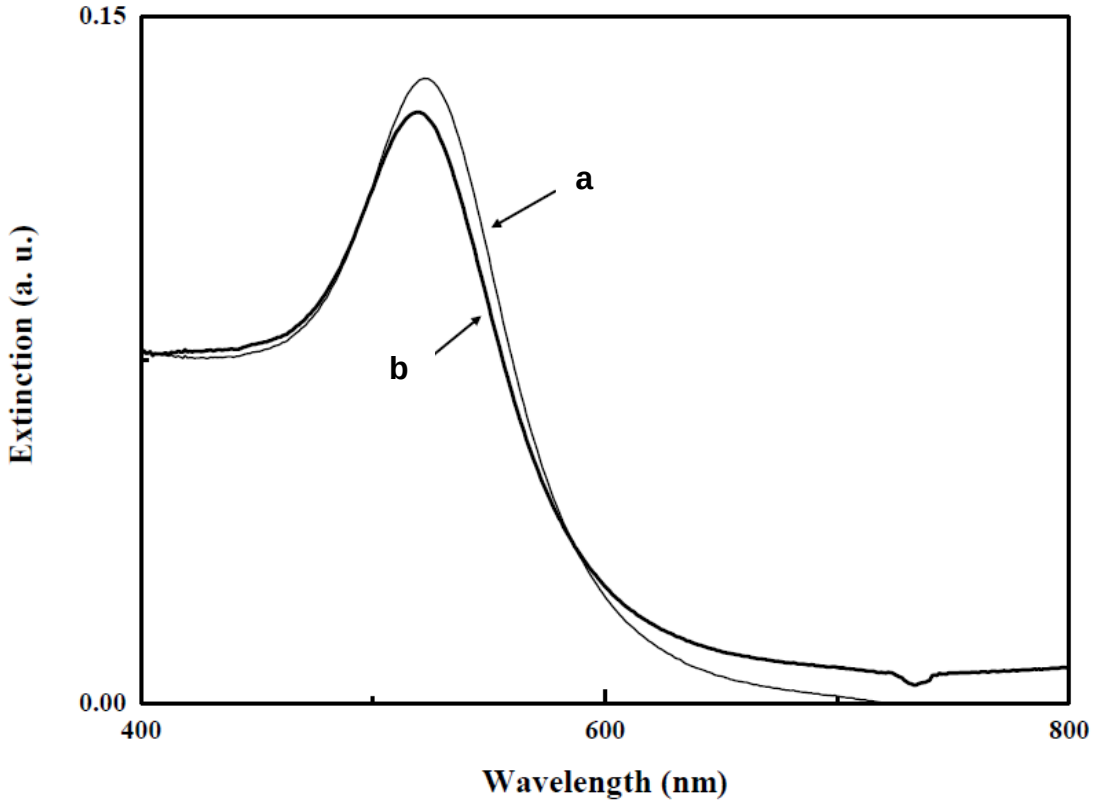

Figure S7. Extinction spectra of solutions of 1 nM PS 40-AuNPs (a) before and (b) after the addition of 50 μM cyanide. PS 40-AuNPs were prepared in deionized water. The incubation time is 30 min.

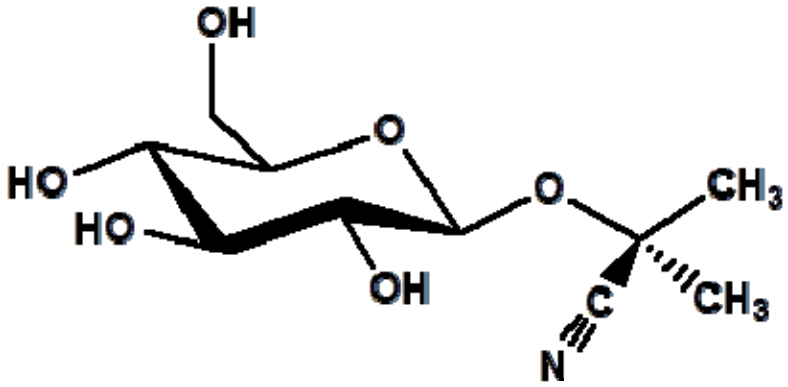

Figure S8. Molecular structure of linamarin.

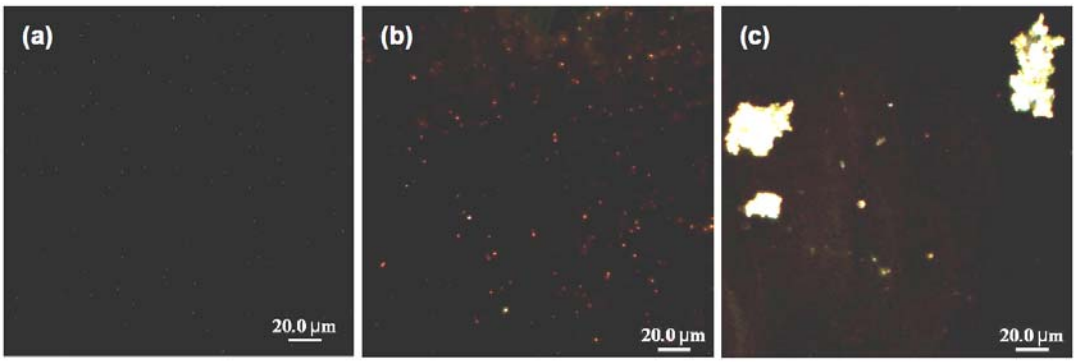

Figure S9. Dark-field images of solutions of PS40-AuNPs in the (a) absence and (b, c) presence of (b) 40 µM cyanide and (c) 40 µM hydrolyzed linamarin

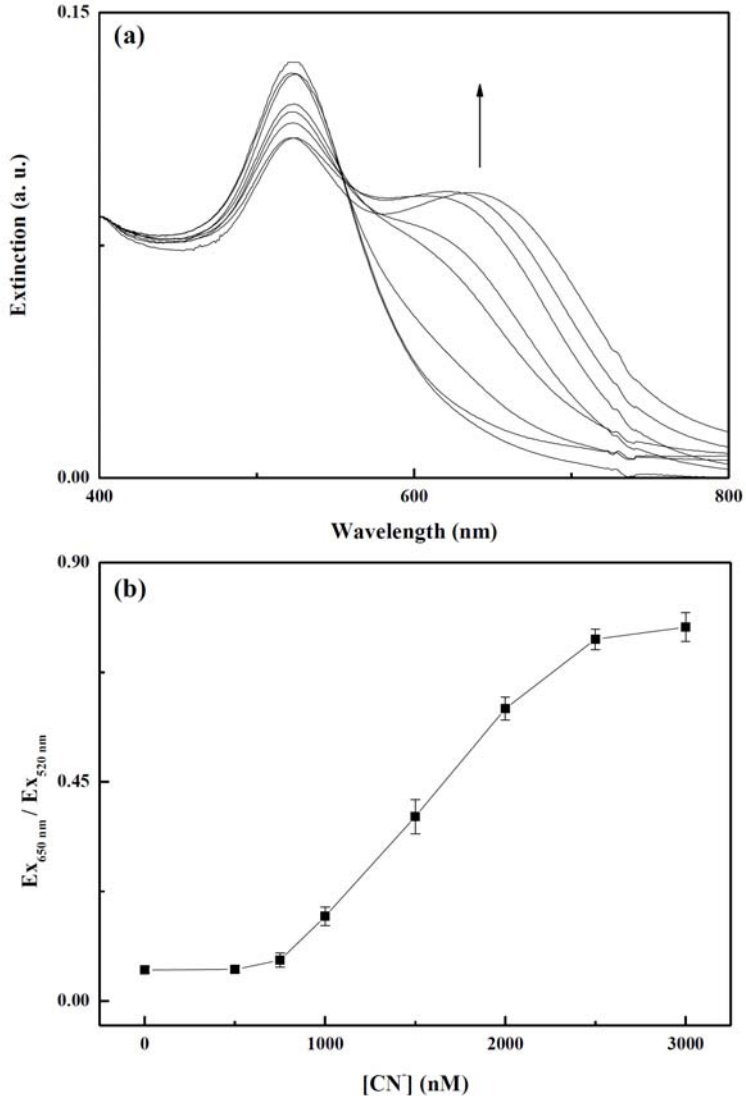

Figure S10. (a) Colorimetric detection of CN^- in tap water by using a solution containing 1 nM PS 40-AuNPs and 5x PBS. Samples of tap water were spiked by standard solutions containing 0–3000 nM CN^-. The arrows indicate the signal changes with increases in analyte concentrations (0, 500, 750, 1000, 1500, 2000, 2500, and 3000 nM)**.** (b) A plot of $Ex_{650\ nm}/Ex_{520\ nm}$ versus the concentrations of CN^- in the range of 0 to 3000 nM. The incubation time is 30 min. The error bars represent standard deviations based on three independent measurements.

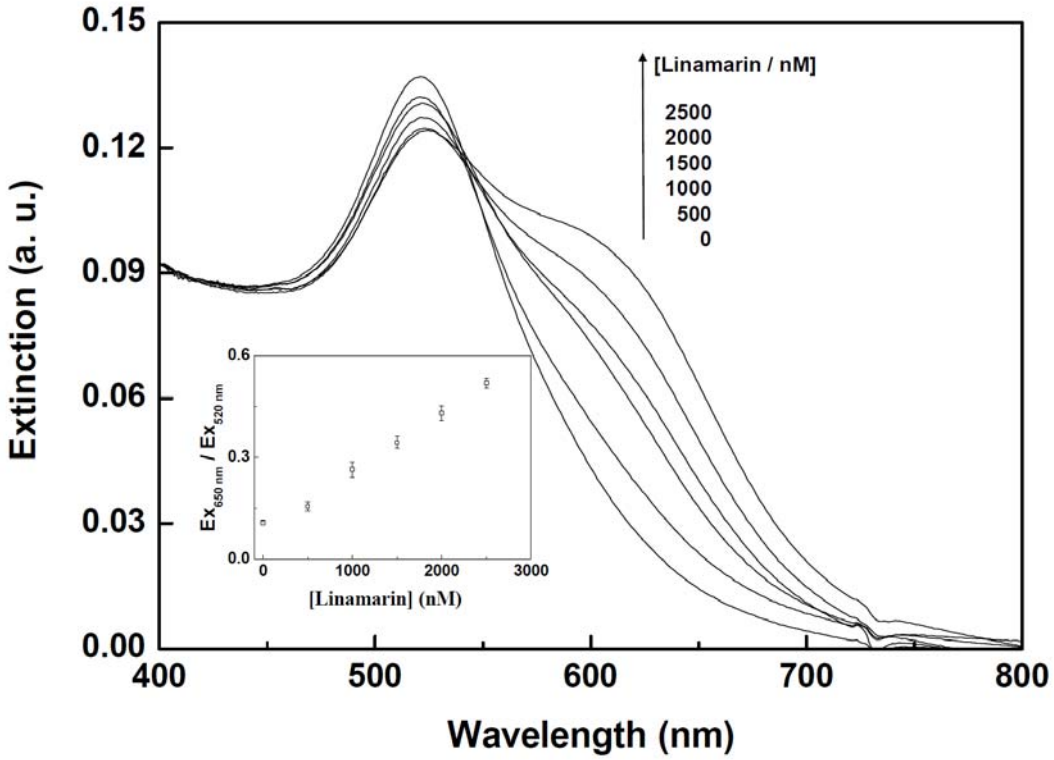

Figure S11. Colorimetric detection of linamarin in cassava root by a solution containing 1 nM PS 40-AuNPs and 5x PBS. Samples of finely ground cassava were spiked by standard solutions containing 0–500 μM. After 1 h incubation at room temperature, the mixture was centrifuged and the obtained supernatant was diluted to 200-fold. The diluted supernatant was added to a solution containing 1 nM PS 40-AuNPs and 5x PBS. The incubation time is 30 min. Inset: A plot of $Ex_{650\ nm}/Ex_{520\ nm}$ as a function of the linamarin concentration. The error bars represent standard deviations based on three independent measurements.