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SUPPORTING INFORMATION

A Simple and Sensitive Colorimetric pH Meter Based on DNA Conformational Switch and Gold Nanoparticle Agrregation

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EXPERIMENTAL SECTION

Chemicals and Materials. Hydrogen tetrachloroaurate(III) ($HAuCl_4.3H_2O$), 99.99%, and sodium citrate dihydrate ($Na_3C_6H_5O_7{\cdot}2H_2O$), 99%, were purchased from Alfa Aesar and used without further purification. All other chemicals were purchased from Sigma-Aldrich and used as supplied. The oligonucleotides used in this paper were synthesized by Sangon Biotechnology Inc. (Shanghai, China). Nanopure water (18.2 MΩ; Millpore Co., USA) was used in all experiments and to prepare all buffers.

Instrumentation. A PHS-3C portable pH meter (Shanghai Precision & Scientific Instrument Co., China) was used to adjust the pH values of all buffers to an accuracy of 0.01 pH unit. The UV-Vis absorption spectra were recorded using a CARY 300 UV/Visible spectrophotometer (Varian Inc., Palo Alto, CA). A JASCO FP-6500 spectrofluorometer (JASCO International Co., LTD., Tokyo, Japan) was used to measure the spectra.

Preparation of AuNPs. AuNPs (~13 nm in diameter) were synthesized by means of sodium citrate reduction of $HAuCl_4$ following a procedure reported previously.[15] Briefly, 50 mL of 1 mM $HAuCl_4$ aqueous solution was brought to a reflux while stirring. 5 mL of 38.8 mM sodium citrate was added rapidly, and the solution was refluxed for an additional 15 min while stirring vigorously. The color changed from pale yellow to deep red, and the solution was allowed to cool to room temperature for use. The concentration of AuNPs solutions were determined using the absorbance values at 520 nm with the extinction coefficient of 2.7×10^8 M^{-1} cm^{-1}.[16]

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pH Sensing Assay. In a typical procedure, 3 μL of 22 μM i-motif DNA or 2.6 μL of 25 μM random DNA was mixed with 200 μL of 11.2 nM AuNPs and 100 μL of 50 mM phosphate buffer at proper pH value for 3 min, followed by addition of 300 μL of 300 mM NaCl. UV-Vis absorption spectra were recorded using a Varian Cary 300 spectrophotometer equipped with a 1-cm path length quartz cell, and light scattering spectra were recorded by synchronously scanning the excitation and emission monochromators from 300 to 700 nm (i.e., $\Delta\lambda=0$) using an FP-6500 spectrofluorometer.

Locally linear approximation A locally linear approximation was built by finding the best collection of straight line segments to fit a collection of training data samples. Each spectrum in this figure was constructed from an average of four spectra. A series of pH-dependent absorbance ratio serves as our "training" data with which we test this parametrization. We then found the piecewise linear curve with k segments that minimizes the mean-squared error over this collection of training data. The (k - 1) breakpoints were found by exhaustively searching all possible gaps between the training data pH values to find the breakpoints that produce the minimum mean-squared error fit. The best-fitting linear segments were found using a standard least-squares method and a two-segment piecewise linear curve was found to fit the pH-ratio curve with high accuracy and minimal complexity for this device output.

Cross validation Cross-validation is an excellent method in chemometrics for building calibration and prediction models. The leave-one-out cross-validation (LOOCV) was used to judge the variation of our estimation procedure by constructing the pH-absorbance ratio model leaving each ratio point out once and testing the variation between the omitted point and the parametrized model, and the resulting pH estimates were used to judge the accuracy and precision of the procedure.

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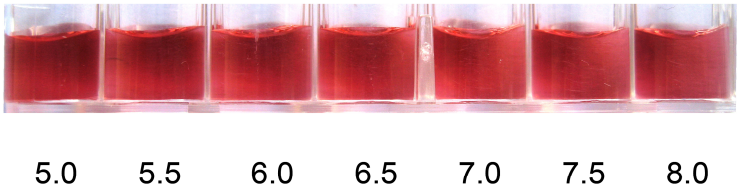

Figure S1. Photograph of random DNA and AuNPs mixed solution at different pH.

References

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