Electronic Supplementary Information

Highly sensitive and selective detection of silver ion and silver nanoparticles in aqueous solution using an oligonucleotide-based fluorogenic probe

Yen-Hsiu, Lin[1] and Wei-Lung Tseng[1, 2]*

1. Department of Chemistry, National Sun Yat-sen University, Taiwan
2. National Sun Yat-sen University-Kaohsiung Medical University Joint Research Center, Kaohsiung, Taiwan

Correspondence: Dr. Wei-Lung Tseng, Department of Chemistry, National Sun Yat-sen University, 70, Lien-hai Road, Kaohsiung, Taiwan 804.

E-mail: tsengwl@mail.nsysu.edu.tw

Fax: 011-886-7-3684046.

Experimental section

Chemicals. HNO_3, H_3PO_4, dimethyl sulfoxide, ethanol and H_2O_2 were purchased from Riedel-deHaën (Seelze, Germany). Tris, Na_2CO_3, NaH_2PO_4, Na_2HPO_4, $NaNO_3$, $NaBH_4$, $AgNO_3$, and 3-morpholinopropanesulfonic acid (MOPS) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All of metal ions were ordered from Acros. A DNA sample was synthesized from Integrated DNA Technology (Coralville, IA). SYBR Green I (SG) was purchased from Molecular Probe Inc. (Portland, OR). Except for the determination of Ag^+ in drinking water, Milli-Q ultrapure water (Milli-pore, Hamburg, Germany) was used in all of the experiments.

Apparatus. The fluorescence spectra of SG were measured using a Hitachi F-4500 fluorometer (Hitachi, Tokyo, Japan) while the excitation wavelength was set at 494 nm.

Synthesis of silver nanoparticles (AgNPs). We prepared citrate-capped AgNPs by means of the chemical reduction of a metal salt precursor ($AgNO_3$) in the liquid phase.[1] To achieve this, we rapidly added 1% w/v trisodium citrate (2 mL) to a solution of 1-mM $AgNO_3$ (100 mL) that was heated under reflux. This heating continued for an additional 30 min. TEM images (not shown) confirmed that the diameter of the AgNPs (density 10.49 g/cm^3) is 50 ± 8 nm, with a standard deviation

of 8.0 nm. To estimate the concentration of AgNPs, we assumed that the reduction from Ag(I) to Ag atoms was 100% complete. The concentration of the original AgNPs is calculated to be 0.42 nM.

Sample preparation. A solution of SG (10000×) was diluted to 250× with dimethyl sulfoxide. The resulting solution was diluted to 6.25× with ultrapure water in order to make a stock solution. Using Beer's law, the concentration of a solution of 6.25× SG is calculated to be 1.23×10^{-5} M. Note that the molar absorption coefficient of SG at the optical wavelength of 494 nm is approximately 73000 M^{-1} cm^{-1}.[2] We added metal ions (0.2–200 μM, 500 μL) to 500 μL of 40 mM MOPS solution (pH 5.5–8.0) containing 100 mM $NaNO_3$, 320 nM SG, and 100 nM C_{20}. To investigate the effect of the DNA length and sequence on our analytical system, we replaced C_{20} with C_5, C_{10}, C_{15}, A_{20}, T_{20}, or 5′-GGG TTA GGG TTA GGG TTA GGG-3′, one at a time. We equilibrated the resulting solutions for the optimum incubation time, and then recorded the fluorescence spectra of the solutions.

Analysis of Real Samples. We collected drinking water from the National Sun Yat-sen University campus. A series of samples were prepared by "spiking" them with standard solutions of Ag^+. We then added these spiked samples (500 μL) to a solution (500 μL) containing 40 mM MOPS, 100 mM $NaNO_3$, 320 nM SG, and 100 nM C_{20}, at pH 7.0. We incubated the resulting solutions for 10 min before measuring

their fluorescence spectra.

This proposed method was utilized to detect 50-nm AgNPs. Different concentrations of AgNPs (128.4–482 nM) were oxidized to Ag^+ with a solution of 1 mM H_2O_2 and 1 μM H_3PO_4. After 20 min, the resulting solution (500 μL) was added to a solution (500 μL) containing 40 mM MOPS, 100 mM $NaNO_3$, 320 nM SG, and 100 nM C_{20}, at pH 7.0. The fluorescence spectra of the resulting solutions were recorded after 10-min incubation.

References

1. R. A. Alvarez-Puebla and R. F. Aroca, *Anal. Chem.*, 2009, **81**, 2280–2285.
2. H. Zipper, H. Brunner, J. Bernhagen, and F. Vitzthum, *Nucleic Acids Research*, 2004, **32**, e103.

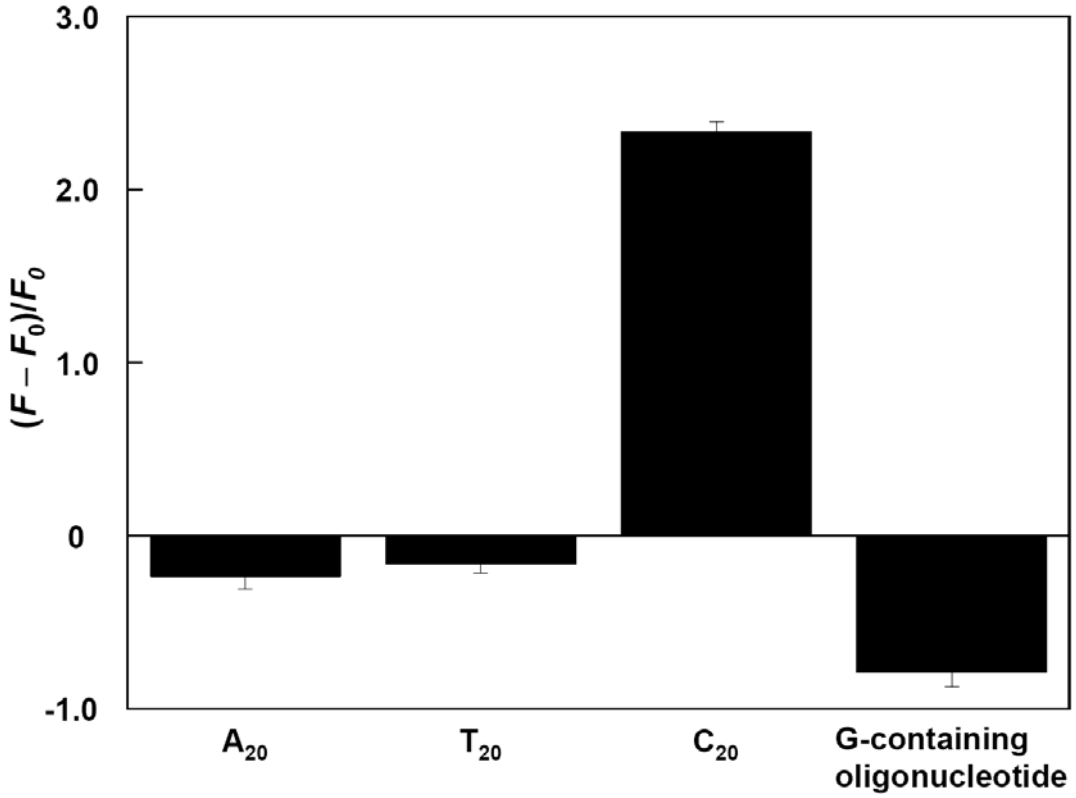

Fig. S1. Relative fluorescence increases [$(F - F_0)/F_0$] at 521 nm of a solution of SG and DNA samples—including A_{20}, T_{20}, C_{20}, and G-containing oligonucleotide (5′-GGG TTA GGG TTA GGG TTA GGG-3′)— on the addition of 1 μM Ag^+. A mixture of 160 nM SG and 50 nM DNA samples was prepared in 20 mM MOPS and 50 mM $NaNO_3$ at pH 7.0. The incubation time is 10 min.

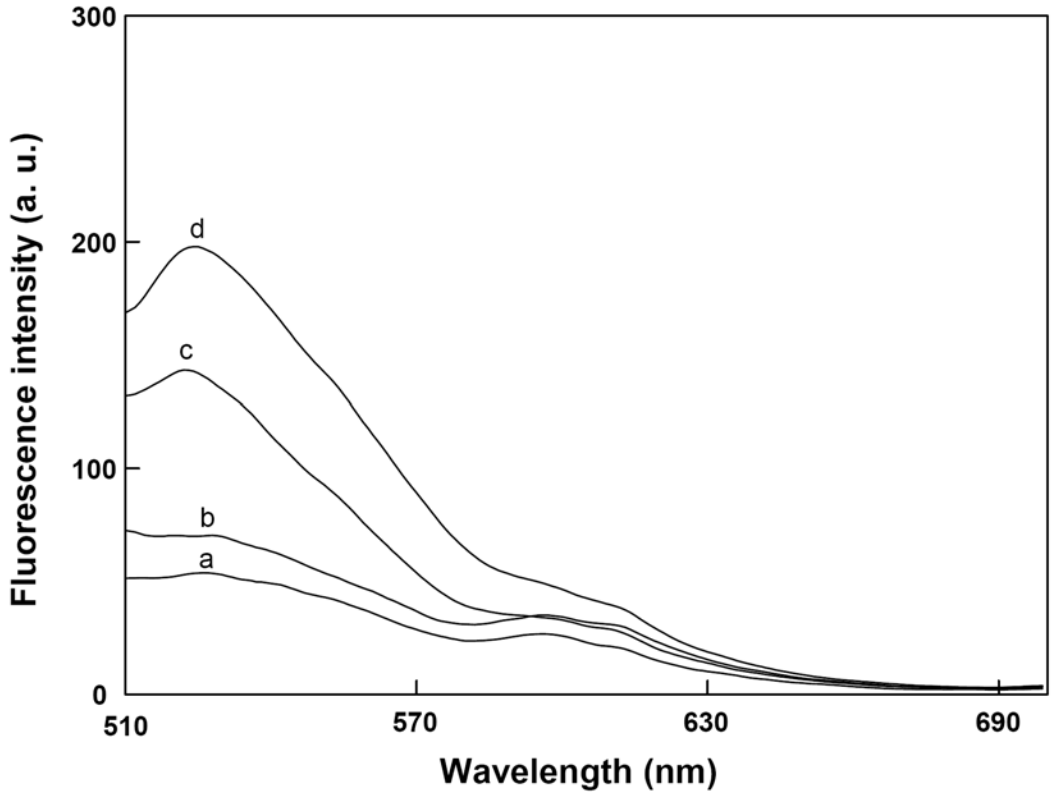

Fig. S2. Fluorescence spectra of a solution containing 160 nM SG, 20 mM MOPS, 50 mM $NaNO_3$, and different concentrations of C_n in the presence of 1 μM Ag^+: (a) 200 nM C_5, (b) 100 nM C_{10}, (c) 67 nM C_{15}, (d) 50 nM C_{20}. The incubation time is 10 min.

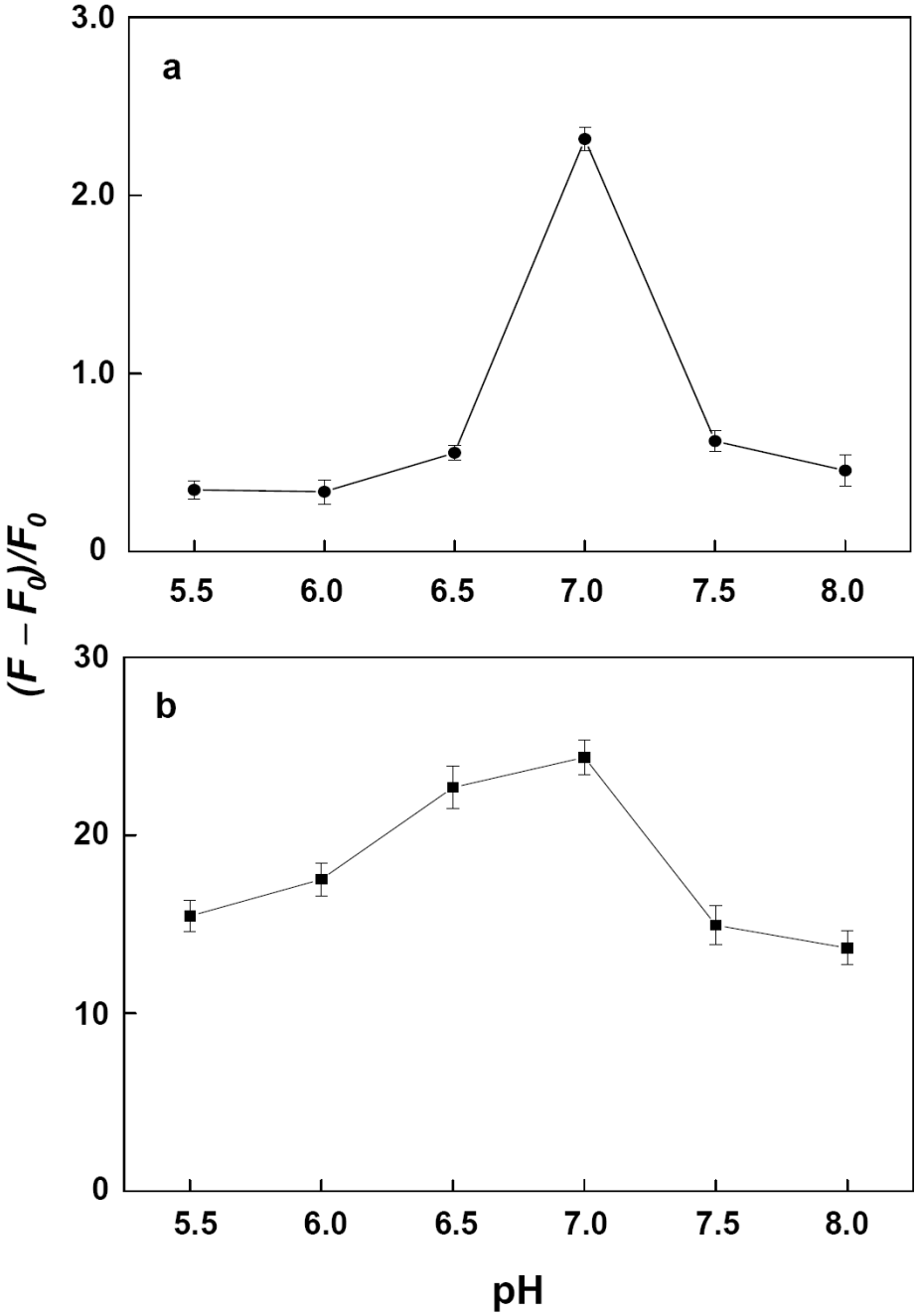

Fig. S3. Effect of the pH on the value of $(F - F_0)/F_0$ at 521 nm of a solution containing 160 nM SG, 20 mM MOPS, 50 mM $NaNO_3$ in the presence of (a) 1 μM Ag^+ and 50 nM C_{20}, (b) 50 nM A_{20} and 50 nM T_{20}. The incubation time is 10 min. (b) We added A_{20} (200 nM, 250 μL) to 500 μL of 40 mM MOPS solution (pH 5.5–8.0) containing 100 mM $NaNO_3$ and 320 nM SG. After 10 min, the resulting solutions were mixed with 250 μL of 200 nM T_{20}. We equilibrated these solutions for 10 min and then recorded the fluorescence spectra of the solutions.

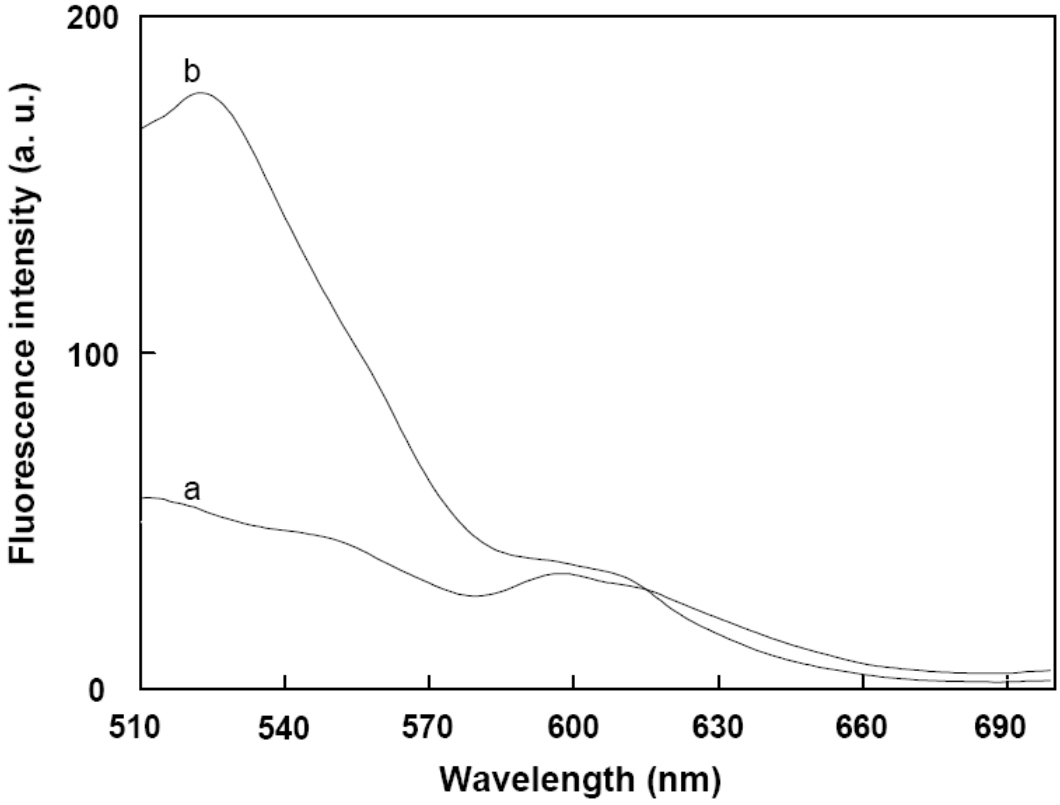

Fig. S4. Fluorescence spectra of a solution containing 160 nM SG, 20 mM MOPS, and 50 nM C_{20} upon the addition of (a) 16 types of metal ions and (b) 16 types of metal ions and Ag^{+}. 16 types of metal ions include Li^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Au^{3+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Cr^{3+}. The concentration of each metal ion is 1 μM. The incubation time is 10 min.

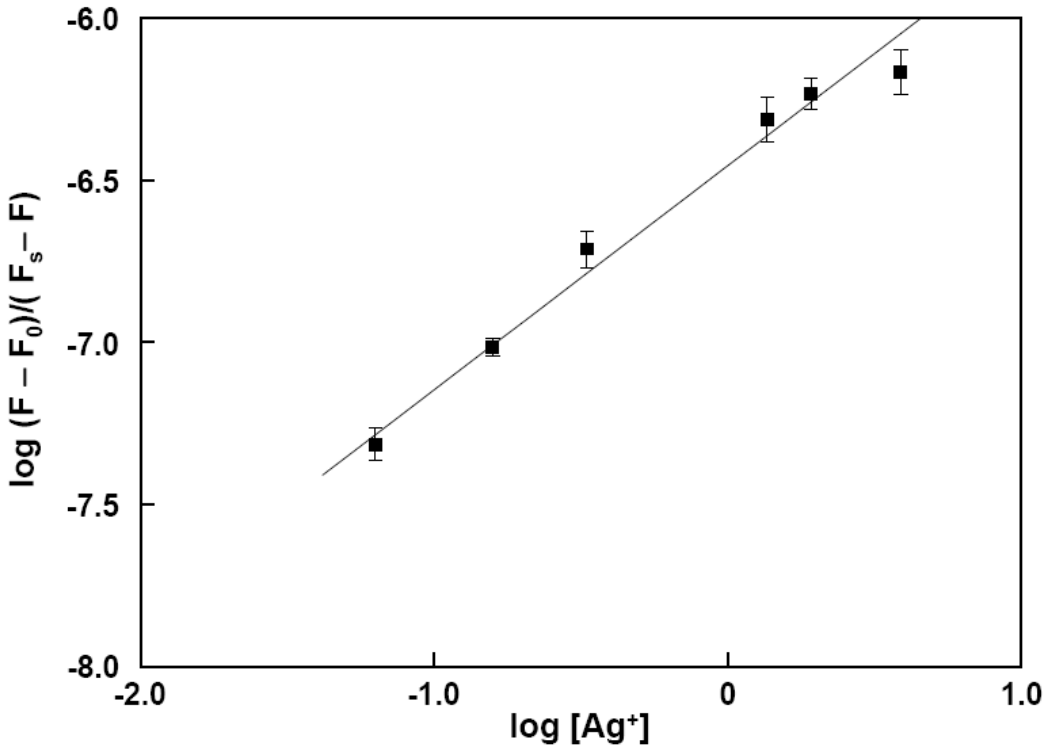

Fig. S5. A plot of of the logarithm of $(F - F_0)/(F_s - F)$ at 521 nm versus the logarithm of the Ag^+ concentration. F_0 and F represent the fluorescence intensity of the SG and C_{20} solution before and after the addition of Ag^+, respectively. F_s represents the fluorescence intensity of the solution of SG and C_{20} saturated with Ag^+.

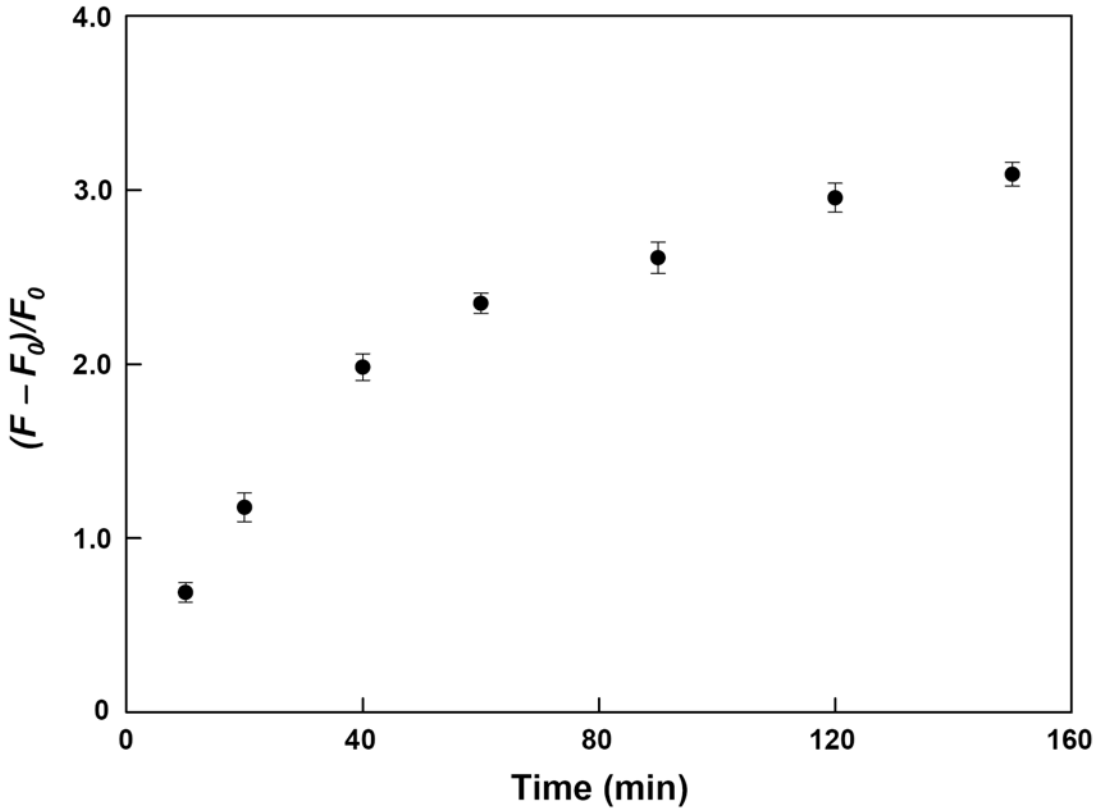

Fig. S6. Change in the value of $(F - F_0)/F_0$ at 521 nm of a solution (160 nM SG, 50 nM C_{20}, 20 mM MOPS and 50 mM $NaNO_3$) upon the addition of H_2O_2-treated AgNPs. A solution of 420 nM AgNPs (50 ± 8 nm) was added to a solution of 1 mM H_2O_2 and 1 μM H_3PO_4.