Electronic Supplementary Information

Silver (I) Ions and Cysteine Detection Based on Photoinduced Electron Transfer Mediated by Cytosine–Ag^{+}–Cytosine Base Pairs

Wan Yi Xie, Wei Tao Huang, Nian Bing Li* and Hong Qun Luo*

Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education), School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P.R. China.

*To whom correspondence should be addressed. Fax: +86-23-68253237.Tel: +86-23-68253237. E-mail: linb@swu.edu.cn. E-mail: luohq@swu.edu.cn.

Experimental section

The oligonucleotides (DNA1: 5'-CTC TCT CTC TCT CTC TCT CTC-FAM-3', DNA2: 5'-CAC ACA CAC ACA CAC ACA CAC-3', DNA3: 5'- GAG AGA GAG AGA GAG AGA GAG -3' and M1DNA3: 5'- CAG AGA GAG AGA GAG AGA GAG -3') were prepared by Sangon Biotechnology Co., Ltd. (Shanghai, China). Single-stranded concentrations were determined by measuring the absorbance at 260 nm. 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), fluorescein, amino acids, glutathione (GSH) and homocysteine (Hcy) were obtained from Aladdin Ltd. (Shanghai, China). The used metal salts, i.e. $AgNO_3$, $Bi(NO_3)_3$, $MgCl_2$, $Cu(NO_3)_2$, $Mn(Ac)_2$, $ZnCl_2$, $CrCl_3$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, $CoCl_2$, $Cd(NO_3)_2$, $FeCl_3$, $FeCl_2$, $CaCl_2$, $NaNO_3$, and $Hg(NO_3)_2$ were of analytical grade and used as received without further purification. Stock solutions of DNA1, DNA2, DNA3, M1DNA3 and $AgNO_3$ were prepared in ultrapure water. All working solutions were prepared with HEPES buffer solution (10 mM, pH 7.4, 200 mM $NaNO_3$). The amino acid solutions were prepared freshly on the day of use.

The fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer (Hitachi, Japan) equipped with a Xenon lamp excitation source. Samples were excited at 480 nm, and emission spectra were collected from 500 to 650 nm at a 1200 nm/min

scan rate. Ultraviolet-visible absorbance spectra were recorded on a Shimadzu UV-2450 spectrophotometer (Suzhou Shimadzu Instrument Co., Ltd., China).

1. Photometric titration experiments

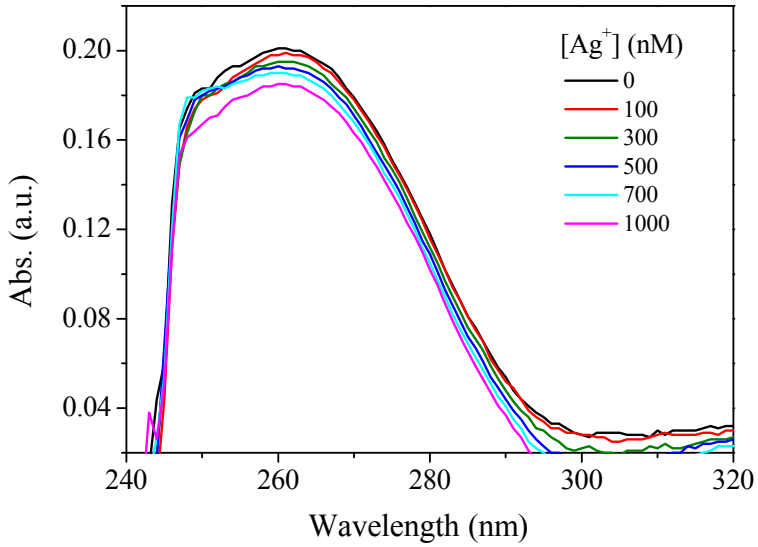

Fig. S1 UV absorption spectra of DNA1/DNA2 (250 nM/250 nM) on addition of $AgNO_3$. Concentration of $AgNO_3$（nM）(from top to bottom): 0, 100, 300, 500, 700, 1000.

2. Reaction time of the addition of Ag^+ ions in the DNA1/DNA2 solution

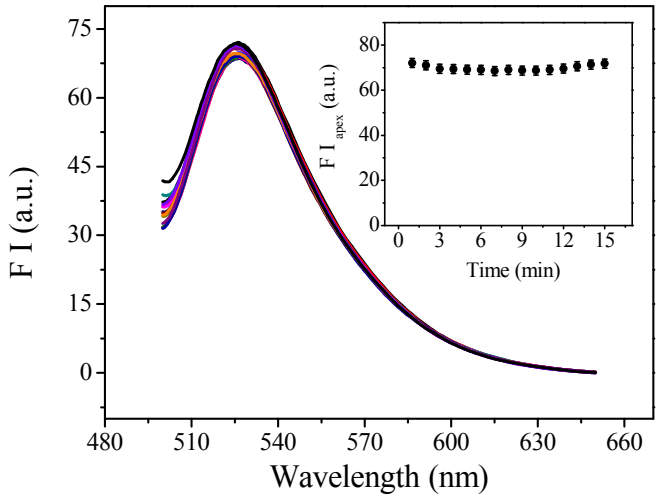

Fig. S2 Fluorescence spectra (λ_{ex} = 480 nm) of DNA1/DNA2 solution (50 nM/50 nM) on addition of $AgNO_3$ (200 nM) at different time.

3. The fluorescence of fluorescein

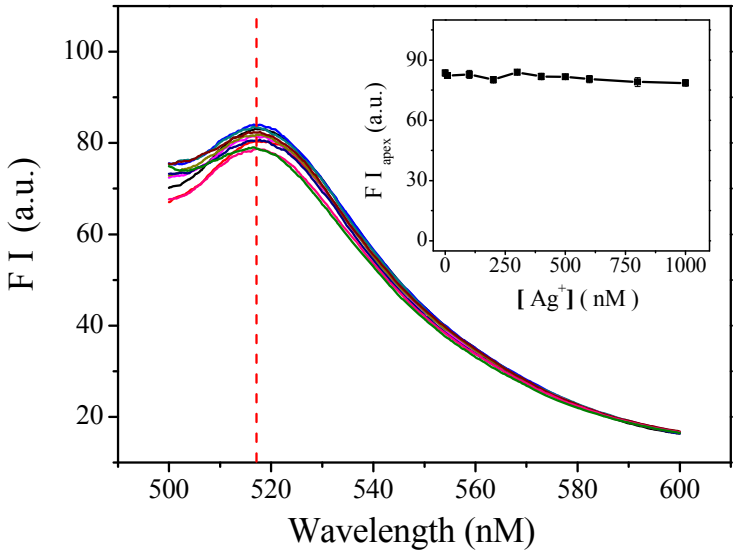

Fig. S3 Fluorescence spectra (λ_{ex} = 480 nm) of fluorescein solution (10 nM) on addition of $AgNO_3$. Inset: fluorescence intensity of fluorescein plotted against the concentration of Ag^+.

4. Absorption spectra of the FAM single-labeled oligonucleotide

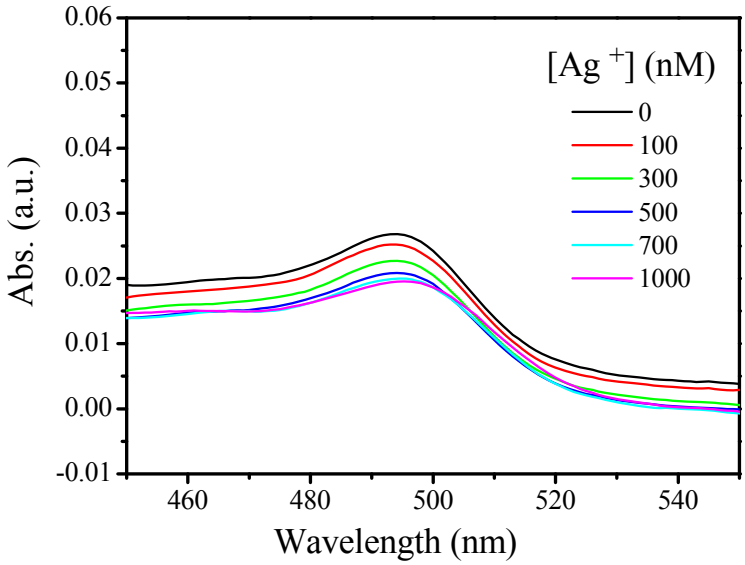

Fig. S4 Absorption spectra of DNA1/DNA2 (250 nM/250 nM) on addition of $AgNO_3$.

5. Fluorescence of DNA1/DNA3 and DNA1/M1DNA3 systems

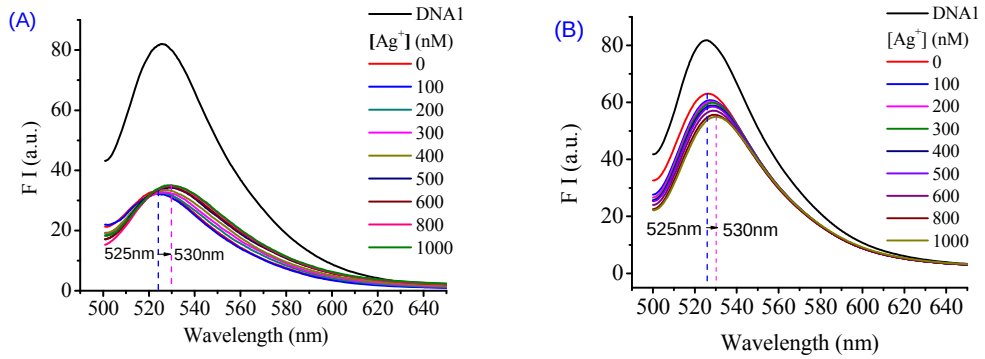

Fig. S5 (A) Fluorescence spectra (λ_{ex} = 480 nm) of DNA1 (50 nM) and DNA1/DNA3 (50 nM/50 nM) on addition of different concentrations of Ag^+. （B）Fluorescence spectra (λ_{ex} = 480 nm) of DNA1 (50 nM) and DNA1/M1DNA3 (50 nM/50 nM) on addition of different concentrations of Ag^+.

6. Reaction time of the addition of Cys in the DNA1/DNA2/ Ag^+ solution

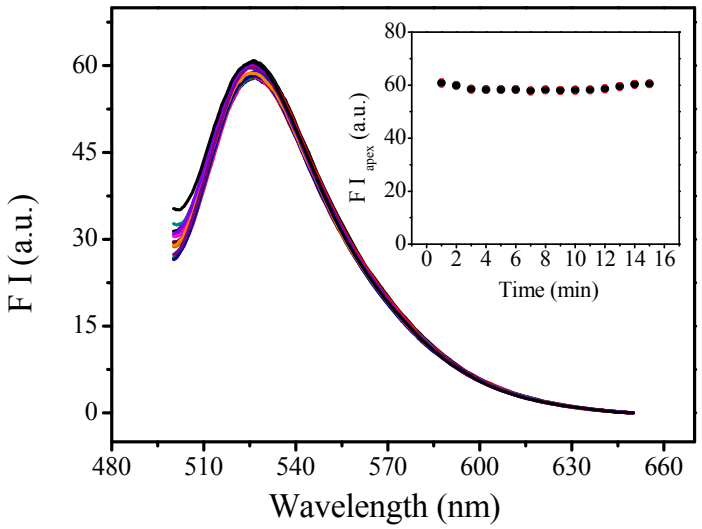

Fig. S6 Fluorescence spectra (λ_{ex} = 480 nm) of DNA1/DNA2/Ag^+ (50 nM/50 nM/800 nM) solution on addition of Cys (40 nM) at different time.

7. Determination of Ag^+ in tap water and river water samples

For tap water, the sample was collected after discharging tap water for about 20 min and boiled for 5 min to remove chlorine. River water sample was obtained from Chia-ling River. The sample collected was first filtered through a 0.2 μM filter membrane to remove oils.

Table1. Detection of Ag^+ in water samples using the proposed method (n = 5)

Sample	Background	Concentration		Recovery (%)	RSD (%)
	Content/nM	Added/nM	Found/nM		
Tap water 1	ND	100	112	112.0	3.06
Tap water 2	ND	200	214	107.0	0.65
Tap water 3	ND	300	320	106.7	2.21
Tap water 4	ND	400	418	104.5	0.74
Chia-ling River 1	ND	100	98	98.0	2.34
Chia-ling River 2	ND	200	204	102.0	0.91
Chia-ling River 3	ND	300	310	103.3	1.51
Chia-ling River 4	ND	400	406	101.5	1.73

ND: not detected

8. Effect of other aminothiols (Hcy and GSH) on the DNA1/DNA2/Ag^+ system

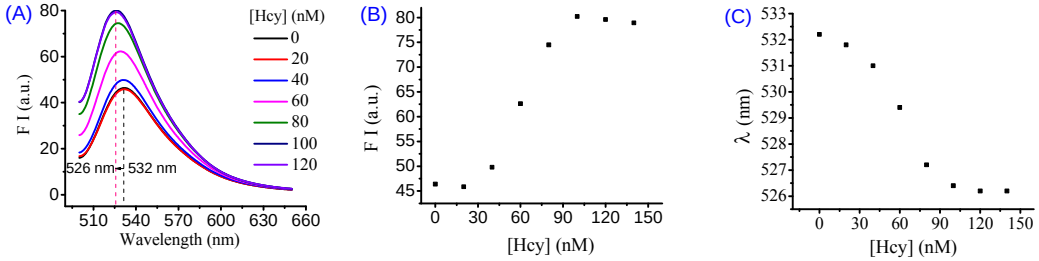

Fig. S7 (A) Fluorescence spectra (λ_{ex} = 480 nm) of DNA1/DNA2/Ag^+ (50 nM/50 nM/800 nM) in the absence and presence of different concentrations of Hcy. (B) The fluorescence intensity at the fluorescence emission peak plotted against the concentration of Hcy. (C) The fluorescence emission wavelength plotted against the concentration of Hcy.

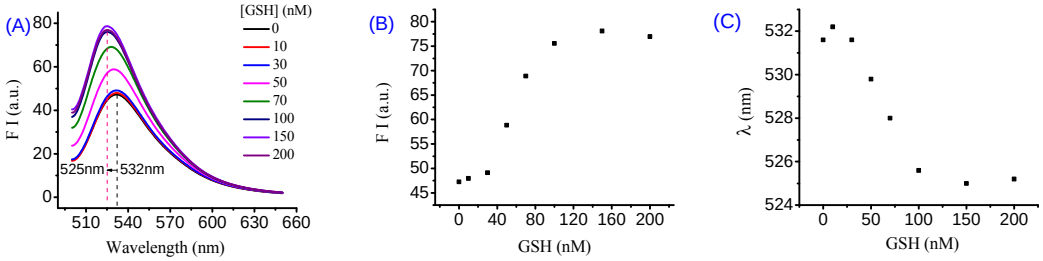

Fig. S8 (A) Fluorescence spectra (λ_{ex} = 480 nm) of DNA1/DNA2/Ag^+ (50 nM/50 nM/800 nM) in the absence and presence of different concentrations of GSH. (B) The fluorescence intensity at the fluorescence emission peak plotted against the concentration of GSH. (C) The fluorescence emission wavelength plotted against the concentration of GSH.