

**Electronic Supplementary Information for**

**Mismatched pyrrolo-dC-modified duplex DNA as a novel probe for  
sensitive detection of silver ions**

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## EXPERIMENTAL SECTION

**Materials.** All DNA oligonucleotides, including pyrrolo-deoxycytosine (pyrrolo-dC)-incorporated DNA, were synthesized and HPLC purified by Genotech Co. (Daejeon, Korea).<sup>1-3</sup> The glutathione (GSH), glutathione disulfide (GSSG) and metal salts ( $\text{Hg}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{CaCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{FeCl}_3$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $(\text{CH}_3\text{COO})_2\text{Mg}$ ,  $\text{CuCl}_2$ ,  $\text{CH}_3\text{COOK}$ ) used in this study were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure DNase/RNase-free distilled water purchased from Invitrogen.

**Silver ion detection procedure.** A solution containing 0.1  $\mu\text{M}$  pyrrolo-dC modified oligonucleotide and 0.12  $\mu\text{M}$  complementary oligonucleotide in a binding buffer (pH 7.9), containing 50 mM potassium acetate, 10 mM magnesium acetate, and 20 mM Tris-acetate, was heated at 80 °C for 5 min, cooled slowly to 30 °C, and incubated at 30 °C for 20 min to form duplex DNA containing the mismatch site. To this solution were added different concentrations of  $\text{Ag}^+$  from a stock solution, which was then incubated at 30 °C for 20 min. The selectivity for  $\text{Ag}^+$  was confirmed by adding other metal ions instead of  $\text{Ag}^+$  following the same procedure. For GSH detection, GSH stock solution was added to the above prepared final solution containing 100 nM  $\text{Ag}^+$ , which was then incubated for 20 min to remove  $\text{Ag}^+$  from the C- $\text{Ag}^+$ -PdC base pairs. The concentration of GSH was 250 nM, which is much lower than that naturally found in human plasma (4  $\mu\text{M}$ ) to confirm that our method possesses much higher detection sensitivity than is required for real clinical or diagnostic application.<sup>[4]</sup>

**Instrumentation.** Fluorescence intensities were measured using a Tecan Infinite M200 pro microplate reader (Mnndorf, Switzerland) and black, 384-well Greiner Bio-One microplates (ref: 781077, Courtaboeuf, France). Excitation was at 350 nm and emission was at 450 nm.

**Table S1.** DNA sequences studied in this work

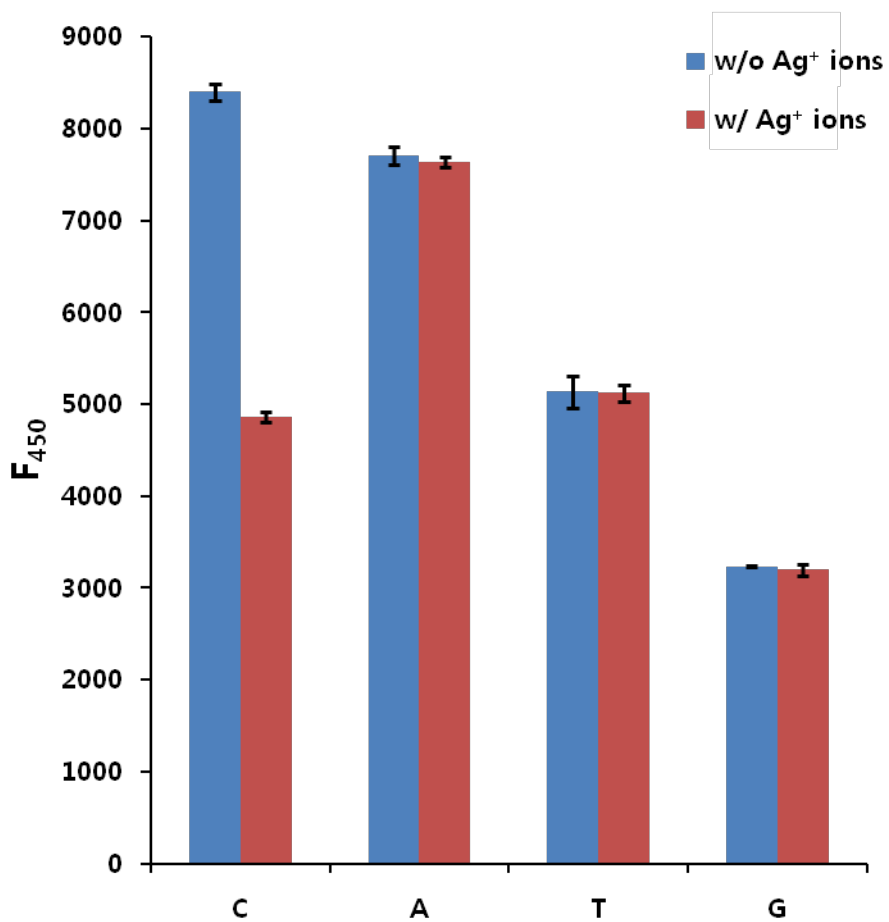
Strand name	DNA sequence (5' → 3')
▪ Oligonucleotides used in Figure 1A, B, 2 and S3	
PdC-modified DNA	GCT TTA GAG TC <b><u>P</u></b> CTG AGA TTT CTG
Complementary DNA (C) <sup>[a]</sup>	CAG AAA TCT CAG C GA CTC TAA AGC
▪ Oligonucleotides used in Figure 1B and S1	
Complementary DNA (A) <sup>[a]</sup>	CAG AAA TCT CAG A GA CTC TAA AGC
Complementary DNA (T) <sup>[a]</sup>	CAG AAA TCT CAG T GA CTC TAA AGC
Complementary DNA (G) <sup>[a]</sup>	CAG AAA TCT CAG G GA CTC TAA AGC
▪ Oligonucleotides used in Figure 1C and S2	
PdC-modified DNA (C) <sup>[b]</sup>	PdC-modified DNA
Complementary DNA	Complementary DNA (C)
PdC-modified DNA (T) <sup>[b]</sup>	GCT TTA GAG TT <b><u>P</u></b> TTG AGA TTT CTG
Complementary DNA	CAG AAA TCT CAA C AA CTC TAA AGC
PdC-modified DNA (A) <sup>[b]</sup>	GCT TTA GAG TA <b><u>P</u></b> ATG AGA TTT CTG
Complementary DNA	CAG AAA TCT CAT C TA CTC TAA AGC
PdC-modified DNA (G) <sup>[b]</sup>	GCT TTA GAG TG <b><u>P</u></b> GTG AGA TTT CTG
Complementary DNA	CAG AAA TCT CAC C CA CTC TAA AGC

[a]: Opposite nucleobase paired with PdC in duplex DNA, which is in blue color.

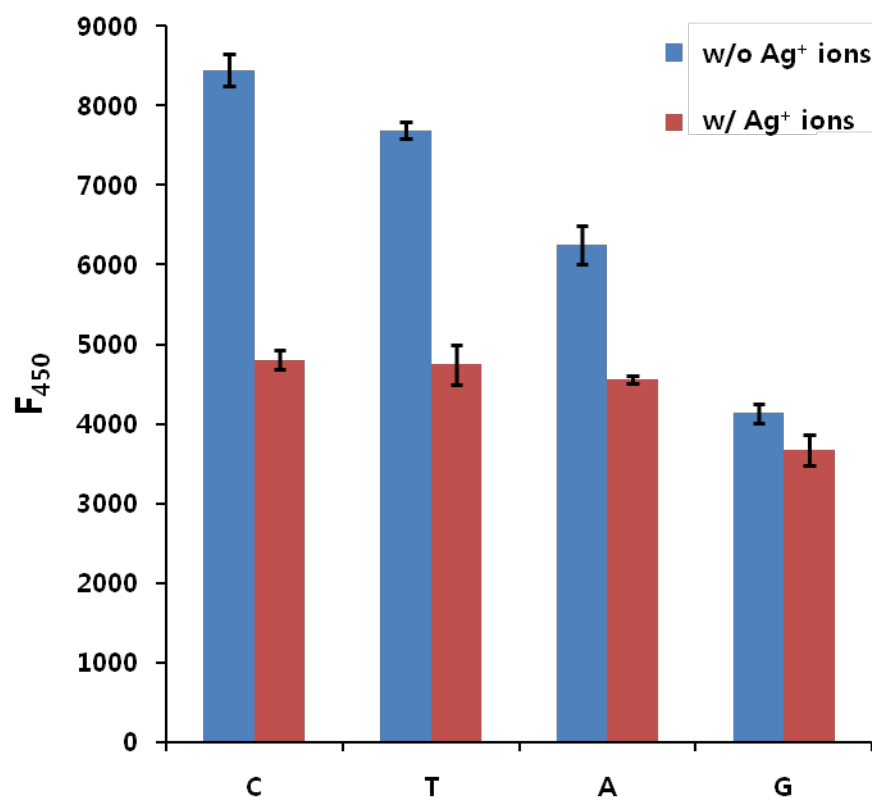
[b]: Flanking nucleobases around the PdC in duplex DNA, which are in red color.

PdC is in bold and underlined. P: pyrrolo-dC (PdC)

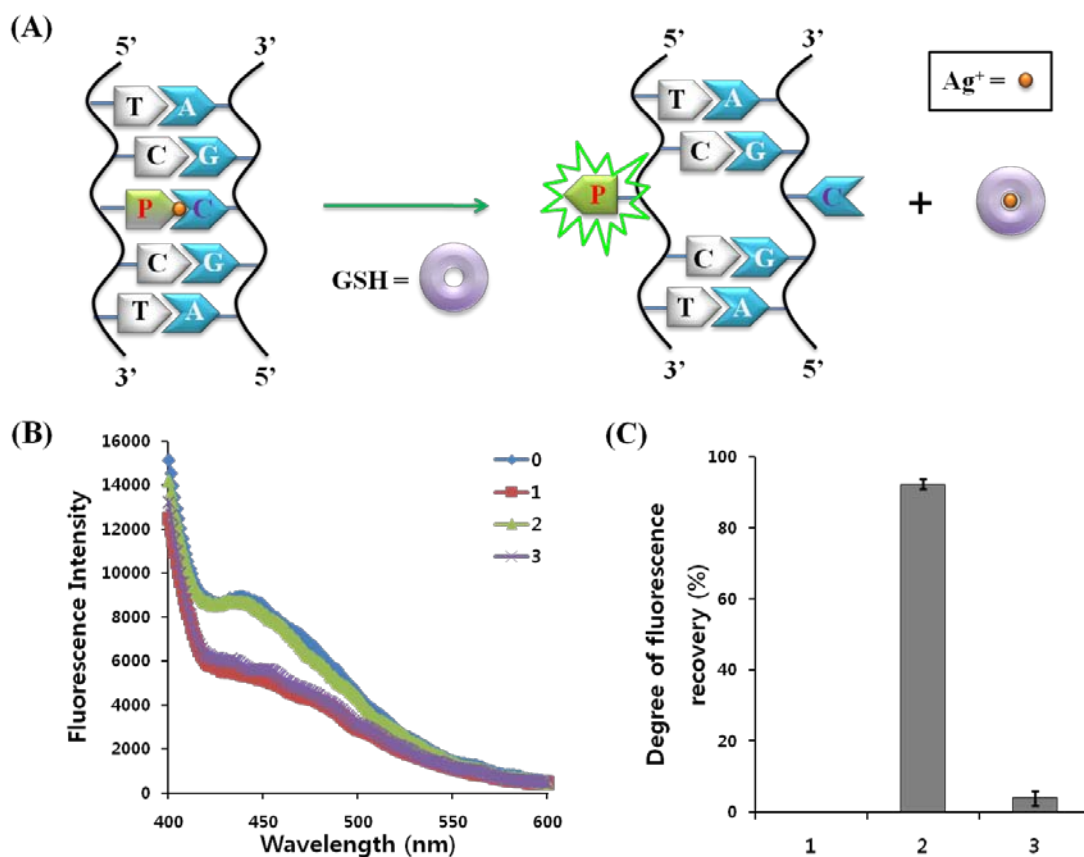
**Fig. S1.** Fluorescence intensities of duplex DNAs containing PdC paired with four different nucleobases (C, A, T, or G) in the absence and presence of silver ions (100 nM).



**Fig. S2.** Fluorescence intensities from duplex DNAs containing PdC-C mismatched base pair with different flanking nucleobases (C: CC, T: TT, A: AA, or G: GG) around the PdC, in the absence and presence of silver ions (100 nM).



**Fig. S3.** Detection of biological thiols. (A) Schematic illustration of the detection strategy for glutathione (GSH), a model biothiol. (B) Fluorescence spectra from mismatched PdC-C modified duplex DNAs in the absence (0) and presence (1) of  $\text{Ag}^+$ . GSH (2) or GSSG (3) was additionally added to the duplex DNA mixed with  $\text{Ag}^+$ . (C) Degree of fluorescence recovery in a histogram form. The degree of fluorescence recovery was defined as  $[(F-F_1)/(F_0-F_1)]$  multiplied by 100, where  $F_0$  and  $F_1$  are originally high fluorescence in the absence of  $\text{Ag}^+$  and  $\text{Ag}^+$ -induced quenched fluorescence in the presence (1) of  $\text{Ag}^+$ , respectively.  $F$  is the fluorescence intensity at 450 nm in the presence of GSH (2) or GSSG (3) together with  $\text{Ag}^+$ . The concentration of  $\text{Ag}^+$ , GSH and GSSG was 100 nM, 250 nM and 250 nM, respectively.



## References

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2. R. Fu, K. Jeon, C. Jung, H. G. Park, *Chem. Commun.* 2011, **47**, 9876.
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