Supporting Information

A Novel Colorimetric Potassium Sensor Based on the Substitution of Lead from G-Quadruplex

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Supplementary figures and discussion

To confirm almost all hairpin DNA 1 transforms to Na^+-stabilized G-quadruplex, the properties of denatured hairpin DNA 1 are tested by CD and UV-Vis measurements and compared with that of hairpin DNA. The results are shown in Fig. S1. It is observed that similar CD spectra and UV-Vis absorption spectra are obtained for hairpin DNA 1 and denatured hairpin DNA 1, which demonstrates almost all hairpin DNA 1 transforms to Na^+-stabilized G-quadruplex in the presence of 140 mM Na^+.

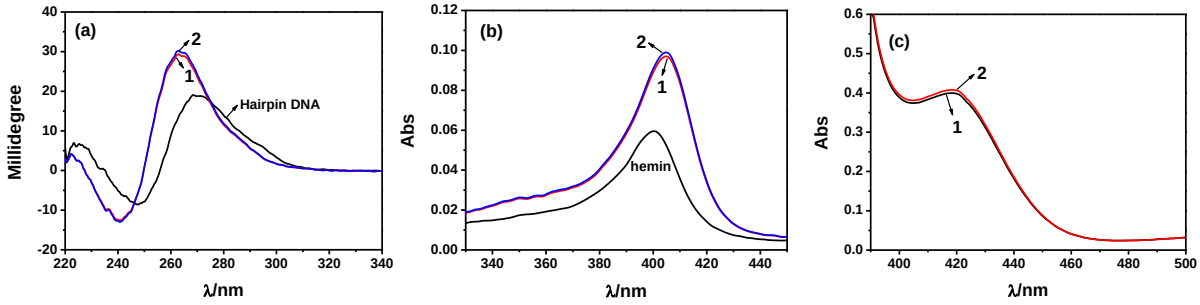


Fig. S1. Properties of hairpin DNA 1 and denatured hairpin DNA 1 in 20 mM Tris-ClO4 buffer (pH = 7.4) containing 140 mM Na^+: (1) hairpin DNA 1; (2) denatured hairpin DNA 1. (a) CD spectra; (b) UV-vis absorption spectra of 1 μM hemin in the absence and presence of hairpin DNA 1 ; (c) UV-Vis absorption spectra of the peroxidation product ($ABTS^{\bullet-}$) at 5 min of the ABTS–H_2O_2 reaction in the presence of 0.1 μM hemin.

In the presence of 140 mM Na^+ (2 h), the hairpin DNA 1 transforming to Na^+-stabilized G-quadruplex as illustrated in Fig. S2. In comparison with Na^+, K^+ has a higher efficiency with regard to stabilizing G-quadruplex due to the K^+-stabilized G-quraduplexes more compact than

that Na^+-stabilized ones.[1] Thus, Na^+-stabilized G-quadruplex converts to K^+-stabilized one upon the addition of K^+. Fig. S2 depicts the conformational switches.

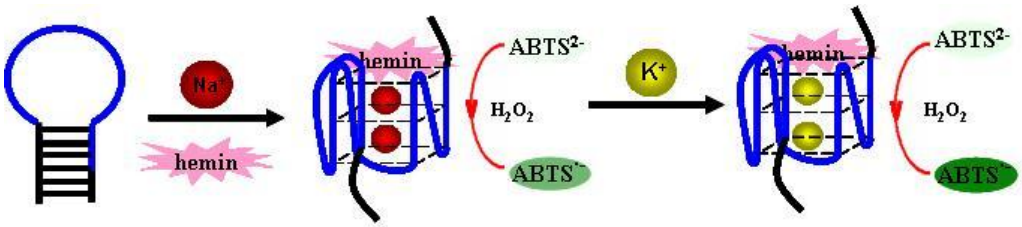


Fig. S2. Schematic of DNA conformational switches and the formed G-quadruplex DNAzyme functions

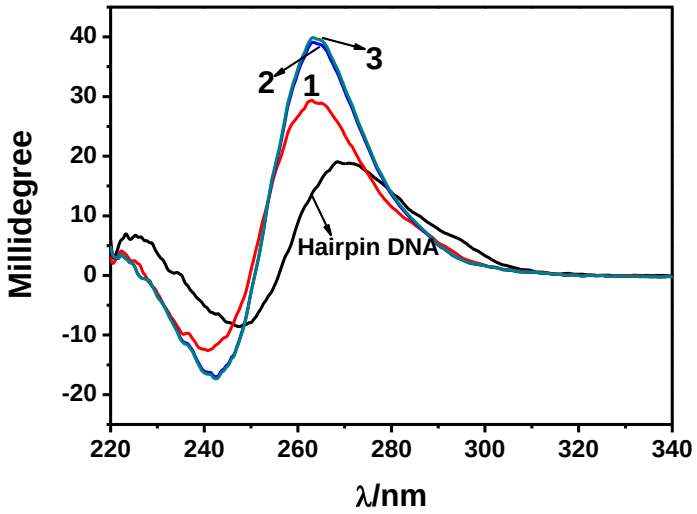


Fig. S3. CD spectra of 4 μM hairpin DNA 1 in 20 mM Tris-ClO4 buffer (pH = 7.4): (1) adding + 140 mM Na^+ for 2 h; (2) adding 10 mM K^+ to (1) for 2 h; (3) adding 10 μM Pb^{2+} to (1) for 2h, then adding 10 mM K^+ for 2h.

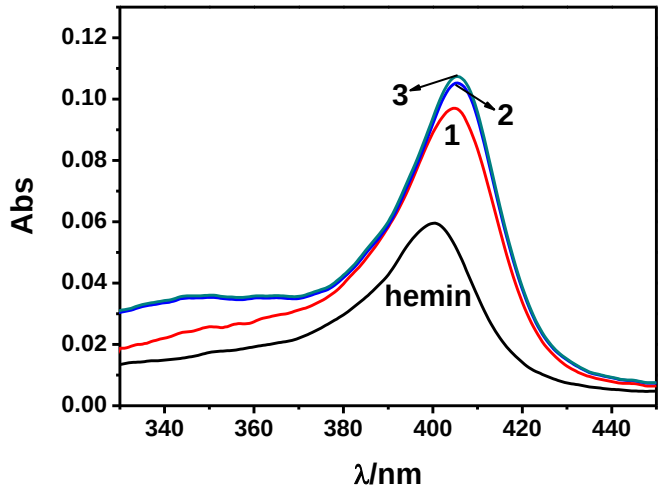


Fig. S4. UV-vis absorption spectra of 1 μM hemin in 20 mM Tris-ClO4 buffer (pH = 7.4) in the absence and presence of (1) 1 μM Hairpin DNA 1 + 140 mM Na^+; (2) 10 mM K^+ + (1); (3) 10 μM Pb^{2+} + (1), then + 10 mM K^+.

To test the irreversibility of the process of K^+ substituting Pb^{2+} to form K^+-stabilized G-quadruplex, we record the UV-Vis absorption spectra of Na^+-stabilized G-quadruplex with sequentially adding K^+ and Pb^{2+} at 2 h intervals to catalyze ABTS–H_2O_2 reaction system. The result is shown in Fig. S5.

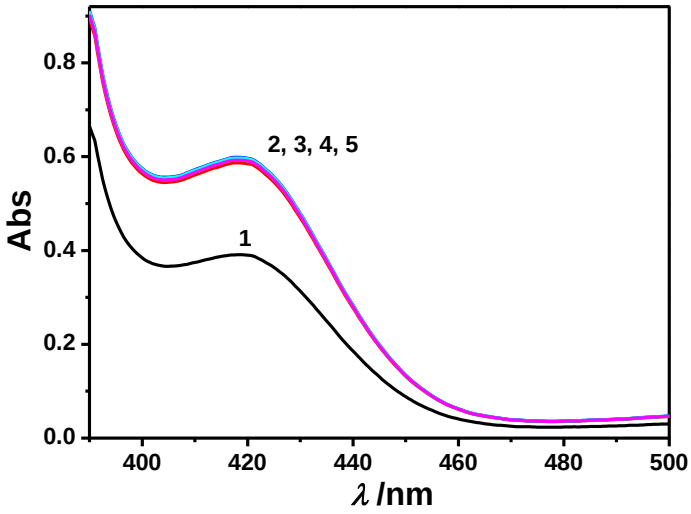
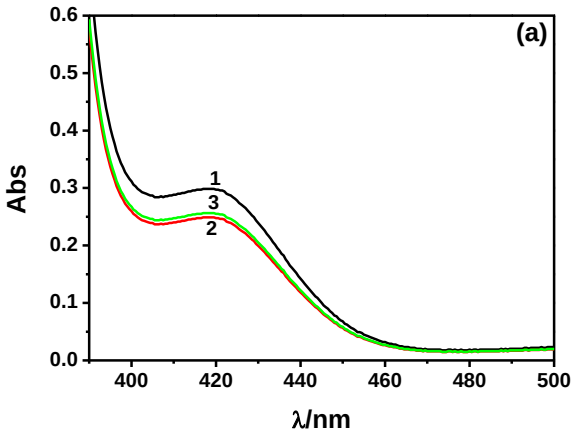


Fig. S5. UV-Vis absorption spectra of the peroxidation product (ABTS•-) at 5 min of the ABTS–H_2O_2 reaction in Tris-ClO4 buffer (pH = 7.4) containing 0.1 μM hemin: (1) 0.1 μM hairpin DNA 1 + 140 mM Na^+; (2) 10 mM K^+ +(1); (3) 100 nM Pb^{2+} + (2); (4) 1 μM Pb^{2+} + (2); (5) 10 μM Pb^{2+} + (2).

To determine if K^+ substituting Pb^{2+} to form K^+-stabilized G-quadruplex is also happened for other G-rich aptamers, we perform the control experiments by UV-Vis measurements with only hairpin DNA 1 instead. The selected aptamers with detailed base sequences are shown in Table S1. As shown in Fig. S6, in the presence of 140 mM Na^+ and 0.1 μM selected aptamer, weak catalytic activity in ABTS-H_2O_2 and hemin system is observed, reflected by weak absorbance of $ABTS^{\bullet-}$ at 420 nm. Upon addition of Pb^{2+}, the absorption intensity at 420 nm is decreased, which is corresponding to Na^+ stabilized G-quadruplex transforming to Pb^{2+}-stabilized one. After the next addition of K^+, nearly no change is observed in absorption intensity. Therefore, we conclude that the processes of K^+ substituting Pb^{2+} do not happen for these selected G-rich aptamers, which is consistent with the reported assays.[1-3]

Table S1 The applied DNA sequence (the underlined are complementary pairs) in control experiments

T30695	5′-GGGTGGGTGGGTGGGT-3′
PS2.M	5′-GTGGGTAGGGCGGGTTGG-3′
Hairpin DNA 7	5′-GTGGGTAGGGCGGGTTGGACCCAC-3′
PW17	5′-GGGTAGGGCGGGTTGGG-3′
Hairpin DNA 8	5′-AAGGGTAGGGCGGGTTGGGACCCTT-3′
Hum21	5′-GGGTTAGGGTTAGGGTTAGGG-3′
Hairpin DNA 9	5′-AAGGGTTAGGGTTAGGGTTAGGGACCCTT-3′



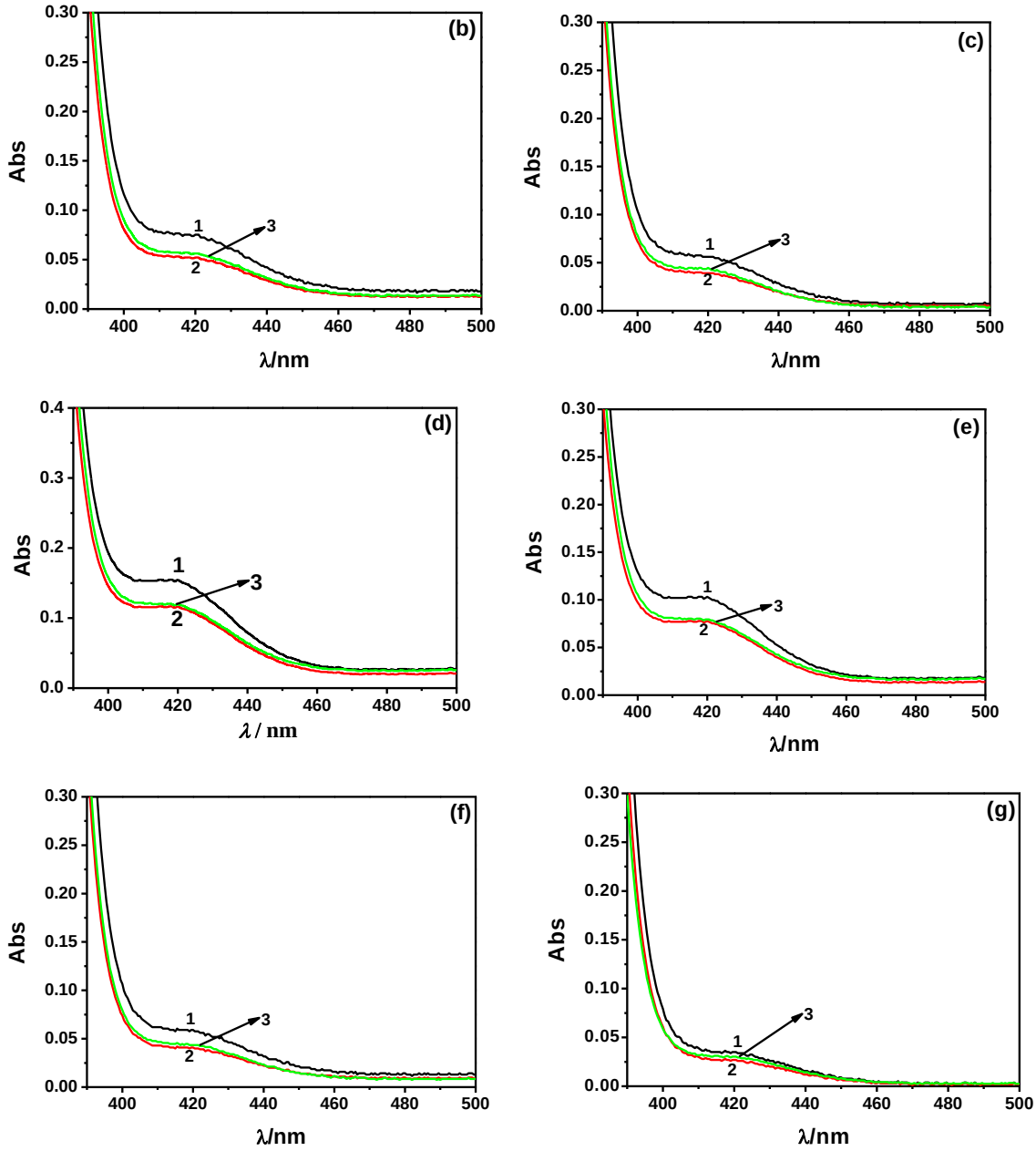


Fig. S6. UV-Vis absorption spectra of the peroxidation product ($ABTS^{\bullet-}$) at 5 min of the ABTS–H_2O_2 reaction in Tris-ClO4 buffer (pH = 7.4) containing 0.1 μM hemin and 0.1 μM G-rich aptamer: (a) T30695, (b) PS2.M; (c) hairpin DNA 7; (d) PW17; (e) hairpin DNA 8; (f) Hum21; (g) hairpin DNA 9. (1) in the presence of 140 mM Na^+, (2) adding 10 μM Pb^{2+} to (1), (3) adding 10 mM K^+ to (2).

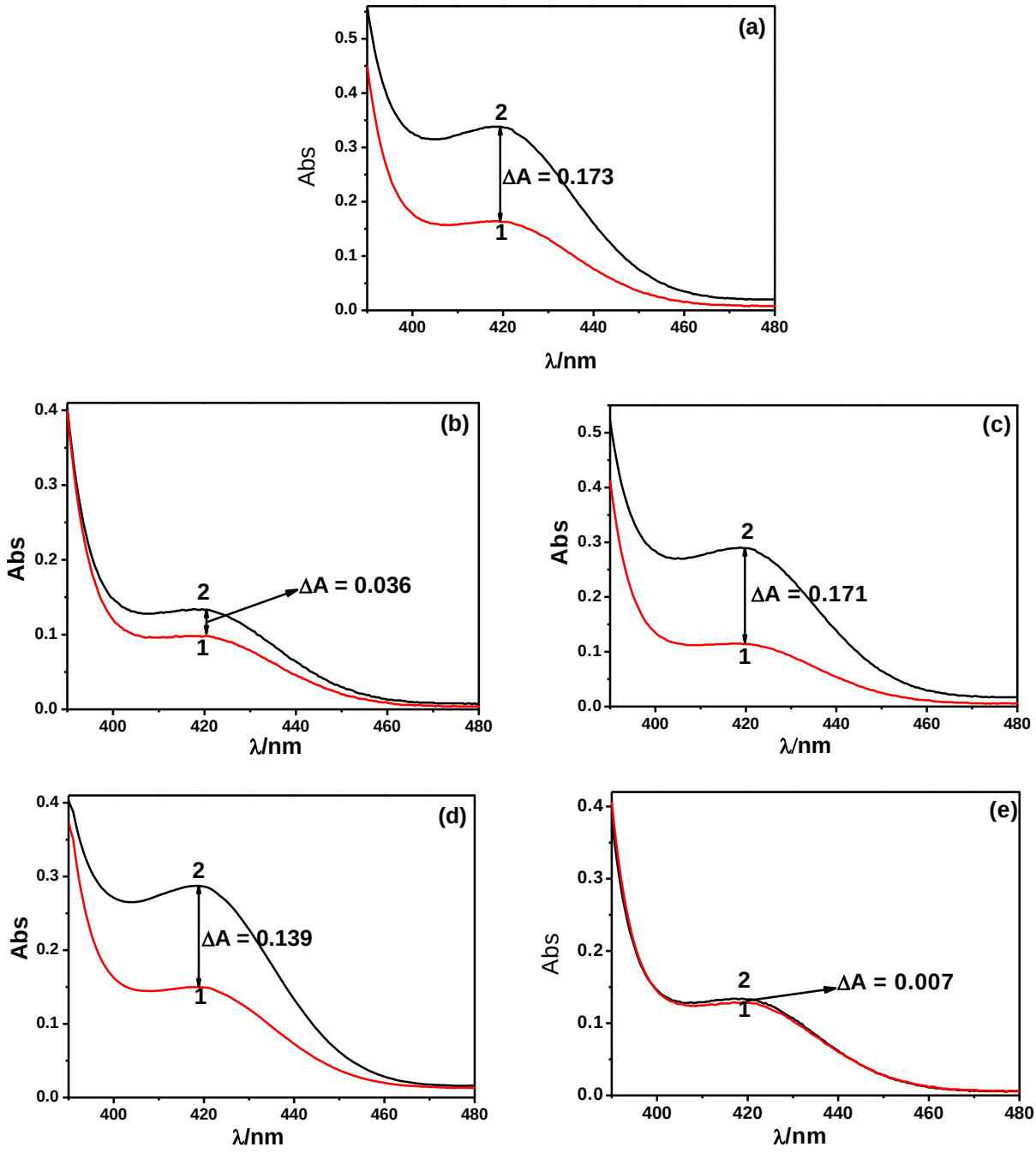


Fig. S7. UV-Vis absorption spectra of the peroxidation product ($ABTS^{\bullet-}$) at 5 min of the ABTS–H_2O_2 reaction in Tris-ClO4 buffer (pH = 7.4) containing 0.1 μM hemin, 140 mM Na^+ and 0.1 μM (a) hairpin DNA 2; (b) hairpin DNA 3; (c) hairpin DNA 4; (d) hairpin DNA 5; (e) hairpin DNA 6: (1) adding 10 μM Pb^{2+}, (2) adding 10 mM K^+ to (1).

To confirm Na^+-stabilized G-quadruplex convert to Pb^{2+}-stabilized one completely, we record the UV-Vis absorption spectra in 0.1 μM Na^+-stabilized G-quadruplex after the addition of different concentrations of Pb^{2+} in the ABTS–H_2O_2 system, and the absorbance at 420 nm is

collected, respectively. The relationship of absorbance intensity at 420 nm and the concentrations of Pb^{2+} is shown in Fig. S8. We can observe that the absorbance at 420 nm gradually decreases as the concentration of Pb^{2+} increases from 10^{-9} M to 10^{-6} M and then remains unchanged when the concentration increases to 10 μM. Thus, 10 μM Pb^{2+} is sufficient for transforming Na^{+}-stabilized G-quadruplex to Pb^{2+}-stabilized one.

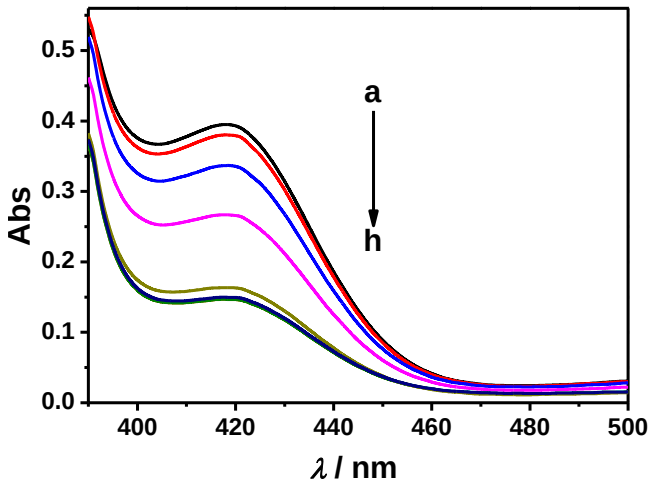


Fig. S8. UV-vis absorption spectra for utilizing 0.1 μM DNAzyme to analyze different concentrations of Pb^{2+}: 0 nM (curve a), 10^{-9} M (curve b), 10^{-8} M (curve c), 10^{-7} M (curve d), 10^{-6} M (curve e), 10^{-5} M (curve f), 5×10^{-4} M (curve g), 10^{-4} M (curve h).

References

(1) Li, T.; Wang, E. K; Dong, S. J. Anal. Chem. 2010, 82, 7576–7580.

(2) Li, T.; Wang, E. K; Dong, S. J. J. Am. Soc. Chem, 2009, 131, 15082-15083.

(3) Li, T.; Dong, S. J; Wang, E. K. J. Am. Soc. Chem, 2010, 132, 13156-13157.