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\textsuperscript{+}-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\textsuperscript{+}-stabilized G-quadruplex in the presence of 140 mM Na\textsuperscript{+}.

Fig. S1. Properties of hairpin DNA 1 and denatured hairpin DNA 1 in 20 mM Tris-ClO\textsubscript{4} buffer (pH = 7.4) containing 140 mM Na\textsuperscript{+}: (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\textsuperscript{•−}) at 5 min of the ABTS–H\textsubscript{2}O\textsubscript{2} reaction in the presence of 0.1 µM hemin.

In the presence of 140 mM Na\textsuperscript{+} (2 h), the hairpin DNA 1 transforming to Na\textsuperscript{+}-stabilized G-quadruplex as illustrated in Fig. S2. In comparison with Na\textsuperscript{+}, K\textsuperscript{+} has a higher efficiency with regard to stabilizing G-quadruplex due to the K\textsuperscript{+}-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](image)

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.](image)
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 Pb²⁺ + (1), then + 10 mM K⁺.

To test the irreversibility of the process of K⁺ substituting Pb²⁺ to form K⁺-stabilized G-quadruplex, we record the UV-Vis absorption spectra of Na⁺-stabilized G-quadruplex with sequentially adding K⁺ and Pb²⁺ at 2 h intervals to catalyze ABTS–H₂O₂ 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–H₂O₂ 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 Pb²⁺ + (2); (4) 1 µM Pb²⁺ + (2); (5) 10 µM Pb²⁺ + (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$_2$O$_2$ and hemin system is observed, reflected by weak absorbance of ABTS$^-$ 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.\textsuperscript{1-3}

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

<table>
<thead>
<tr>
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<th>Applied DNA sequence (the underlined are complementary pairs)</th>
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<tbody>
<tr>
<td>T30695</td>
<td>5$'$-GGGTGGGTGGGTGGGT-3$'$</td>
</tr>
<tr>
<td>PS2.M</td>
<td>5$'$-GTGGGTAGGGCGGGTTGG-3$'$</td>
</tr>
<tr>
<td>Hairpin DNA 7</td>
<td>5$'$-GTGGGTAGGGCGGGTTGGACCCAC-3$'$</td>
</tr>
<tr>
<td>PW17</td>
<td>5$'$-GGGTAGGGCGGGTTGGG-3$'$</td>
</tr>
<tr>
<td>Hairpin DNA 8</td>
<td>5$'$-AAGGGTAGGGCGGGTTGGACCCTT-3$'$</td>
</tr>
<tr>
<td>Hum21</td>
<td>5$'$-GGGTAGGGTTAGGGTTAGGG-3$'$</td>
</tr>
<tr>
<td>Hairpin DNA 9</td>
<td>5$'$-AAGGGTAGGGTTAGGGTTAGGGACCCTT-3$'$</td>
</tr>
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![Absorption spectrum](https://example.com/absorption_spectrum.png)
Fig. S6. UV-Vis absorption spectra of the peroxidation product (ABTS\(^{\cdot}\)) at 5 min of the ABTS–H\(_2\)O\(_2\) reaction in Tris-ClO\(_4\) 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\(^{\cdot+}\)) at 5 min of the ABTS–H\(_2\)O\(_2\) reaction in Tris-ClO\(_4\) 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\(_2\)O\(_2\) 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.

![UV-vis absorption spectra](image)

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), $5\times10^{-4}$ M (curve g), $10^{-4}$ M (curve h).

**References**

