Electronic Supplementary Information

Label-free fluorescent sensor for mercury (II) based on target-induced structure-switching G-quadruplex

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Experimental section

Chemicals and Materials

The oligonucleotides, G4D (5'-GGGTTGGGTTGGGTTGGG-3'), was synthesized and HPLC purified by TaKaRa Biotechnology Co., Ltd (Dalian, China). Tris(hydroxymethyl)aminomethane (Tris), protoporphyrin IX (PPIX), and Mercury(II) perchlorate were purchased from Sigma (St. Louis, MO, USA). All other chemicals were of analytical grade and used without further purification. Tris-HAc buffer (50 mM, pH 8) was used throughout the experiments. Deionized water was used for the preparation of aqueous solution.

Sensor preparation

The DNA solution was heated at 90℃ for 10 min to dissociate any intermolecular interaction, and gradually cooled to room temperature. Then, freshly prepared PPIX solution, K^+ solution, and Hg^{2+} of various concentrations were added into the DNA solution. The mixture was kept at room temperature in the dark for 2 h to achieve structural changes and PPIX binding, and then the fluorescence intensity was measured.

Circular dichroism analysis

A MOS-450 Circular Dichroism Spectroscopy (Bio-Logic, France) was utilized to collect CD spectra of G4D solution at room temperature. The optical chamber (1 mm pathlength, 300 μL volume) was deoxygenated with dry purified nitrogen (99.99%) before use and the nitrogen atmosphere was kept during experiment. Three scans (75 nm min^{-1}) from 230 to 320 nm at 0.125 nm intervals were accumulated and averaged. The background of the buffer solution was subtracted from the CD data.

Fluorescence spectroscopic analysis

The fluorescence emission spectra of G-quadruplex DNA/PPIX complex in the Tris-HAc buffer were collected from 575 to 725 nm using an F-2500 Spectrofluorometer (Hitachi, Japan) at room temperature. The excitation wavelength was set at 410 nm.

UV-Visible spectroscopic analysis

The binding interactions between G-quadruplex and PPIX in the Tris-HAc buffer were investigated by UV-Vis absorption spectroscopy, which are reflected by the hyperchromicity of the Soret band of PPIX. The absorption spectra were collected with a Lambda 35 UV/Vis Spectrophotometer (Perkin-Elmer, American) in the wavelength range from 300 to 500 nm.

Binding assays

Fluorescence titration measurement was performed by keeping the concentration of PPIX at 0.5 μM while varying the G4D concentrations in Tris-HAc buffer. After incubation for 2 h, the fluorescence intensity at 632 nm of these mixtures was measured to plot binding isotherm of PPIX to G4D. According to the binding isotherm, Scatchard plot was drawn[1], from which the PPIX binding affinity (K_d) and binding stoichiometry (n) are obtained.

Detection of Hg^{2+} in real samples

Samples of lake water were collected from the Wenying Lake and our laboratory, respectively. All samples were first filtered through a 0.22 μm filter membrane to remove insoluble substances. For Hg^{2+} detection, 100 μL of G4D, 100 μL of PPIX, 100 μL of Hg^{2+} with various concentrations and 100 μL of buffer (500 mM Tris–HAc, 1 M KCl, pH 8.0) were added to 600 μL of water sample solution. Other procedures were the same as that described above.

Supplementary Figures

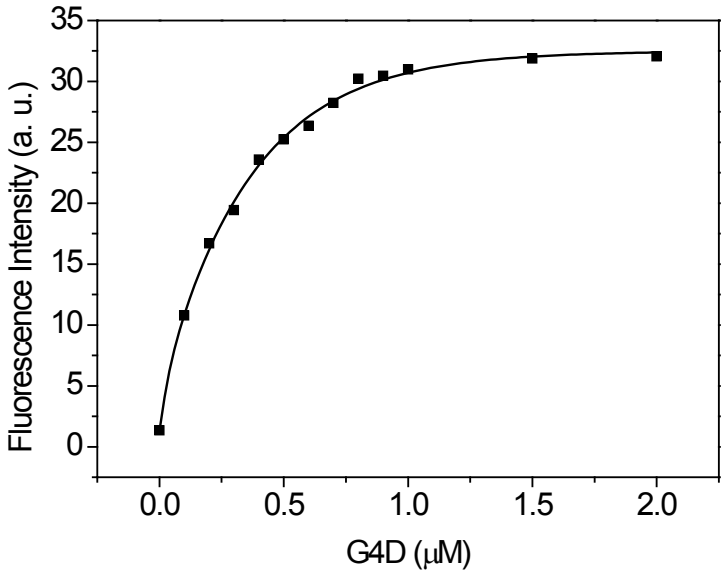

Fig. s1. Fluorescence titration of PPIX (0.5 μM) with G4D in 50 mM Tris- HAc, 100 mM KCl buffer at pH 8.

Table s1 Performance comparison of this work with other oligonucleotide-based optical sensor for Hg^{2+} detection.

Analytical method	Sensor mode	Operation	Linear range	Detection limit	Real sample	Ref.
Fluorescence	Turn-off	Simple, label free	0.05-5 μM	25 nM	Lake water Tap water	This work
Fluorescence	Turn-off	Simple, labeled	40-100 nM	40 nM	Not reported	2
Fluorescence	Turn-on	Complex, labeled	0.05-2.4 μM	10 nM	Human urine	3
Fluorescence	Turn-on	Complex, labeled	0-100 ppb	4 ppb	Not reported	4
Fluorescence	Turn-on	Simple, labeled	10-400 nM	2.5 nM	River water	5
Fluorescence	Turn-on	Simple, label free	10-300 nM	10 nM	Lake water Tap water	6
Fluorescence	Turn-on	Simple, labeled	0.05-8 μM	14.5 nM	Not reported	7
Fluorescence	Turn-off	Simple, labeled	10-200 nM	5 nM	Soil and pond water	8
Fluorescence	Turn-off	Complex, labeled	Not reported	10 nM	Not reported	9
Fluorescence	Turn-on	Simple, label free	10-200 nM	3 nM	Pond water	10
Fluorescence	Turn-on	Simple, labeled	2.4-20 nM	2.4 nM	Not reported	11
Fluorescence	Turn-off	Simple, labeled	Not reported	0.67 nM	River water	12
Naked eye	Turn-on	Simple, labeled	Not reported	1 μM	Not reported	13
Colorimetric	Turn-on	Complex, labeled	Not reported	100 nM	Not reported	14
Colorimetric	Turn-off	Simple, label free	50-2500 nM	50 nM	Freshwater and seawater	15
Visual fluorescence	Turn-on	Complex, label free	75-1000 nM	75 nM	Lake water	16

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