Supplementary Information

Label-free DNAzyme-based fluorescing molecular switch for sensitive and selective detection of lead ion

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Experimental Details.

Materials. The 17E DNAzyme (5'-CAT CTC TTC TCC GAG CCG GTC GAA ATA GTG AGT-3', abbreviated as 17E) and the cleavage substrate (5'-ACT CAC TAT *rA* GGA AGA GAT G-3', abbreviated as 17S) were synthesized by Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). The concentration of oligonucleotides was determined using the 256 nm UV absorbance and the corresponding extinction coefficient. Quant-iT^{TM} Picogreen$^{®}$ dsDNA reagent was purchased from Invitrogen Co. Ltd. (Eugene, Oregon, USA), supplied in DMSO solution and kept at ≤ -20 °C. A working solution was prepared before an experiment by diluting the stock 200× in tris-HCl buffer. All the other chemicals were of analytical reagent grade and were

used as received without further purification. Solutions were prepared with deionized water processed with a Milli-Q ultra-high purity water system (Millipore, Bedford, MA, USA). 20 mM tris-HCl buffer (140 mM NaCl, 5.0 mM KCl, pH 7.4) was used throughout the experiments.

Instrumentation. Fluorescent emission spectra were recorded on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France). A JASCO J–820 spectropolarimeter (Tokyo, Japan) was utilized to collect the circular dichroism (CD) spectra in the tris–HCl buffer. The optical chamber (1 cm path length, 1 mL volume) was deoxygenated with dry purified nitrogen (99.99%) before use and kept the nitrogen atmosphere during experiments. The background of the buffer solution was subtracted from the CD data automatically.

Performance of Pb^{2+} Detection. (I) The formation of the 17E-17S duplex. 1.0 μM 17E-17S duplex in tris-HCl buffer was prepared by hybridizing 17E DNAzyme and its substrate 17S with a molar ratio of 1:1 at 90 °C for 5 min, then slowly cooling to room temperature. (II) The cleavage reaction. 50 μL of 1.0 μM 17E-17S duplex was mixed with 25μL Pb^{2+} solution of an appropriate concentration in tris-HCl buffer and held for 10 min. (III) Fluorescent detection using Picogreen. The prepared solution of Picogreen was mixed with the solution of (II) and incubated for 5.0 min at room temperature, and then the fluorescence intensity was measured. The final concentration of the 17E-17S duplex in the working solution is 100 nM.

Preparation of soil samples. Soil samples were collected from different locations in South Lake Park in Changchun, Jilin, China. Soil samples were mixed and

homogenized, air-dried and filtrated through 250 mesh nylon fiber sieves. Soil sample (0.2013 g), 3.0 mL HCl, 1.0 mL HNO_3 and 2.0 mL HF were added into the Polytetrafluoroethylene (PTFE) crucible, and then incubated at 120 °C for 4.0 h. After cooling, 1.0 mL $HClO_4$ was added into the PTFE crucible; the crucible was opened and heated at 180 °C to dryness on a hot plate. 0.5 mL $HClO_4$ was then added and the crucible was again heated at 180 °C to dryness on hot plate, the residue is dark brown. The residue was dissolved in 1.0 mL HNO_3, finally, the volume was adjusted to 25 mL. Pb^{2+} was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), the concentration is 30.7 μg/g.

Supplementary Figures

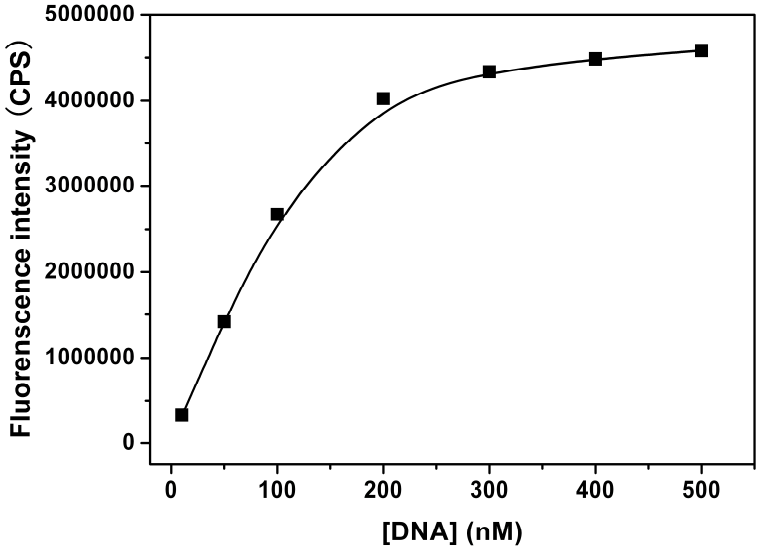

Fig. S1. Fluorescence intensity of PG in the presence of 10-500 nM 17E-17S duplex. Fluorescence intensity was recorded at 525 nm with an excitation wavelength of 480 nm.

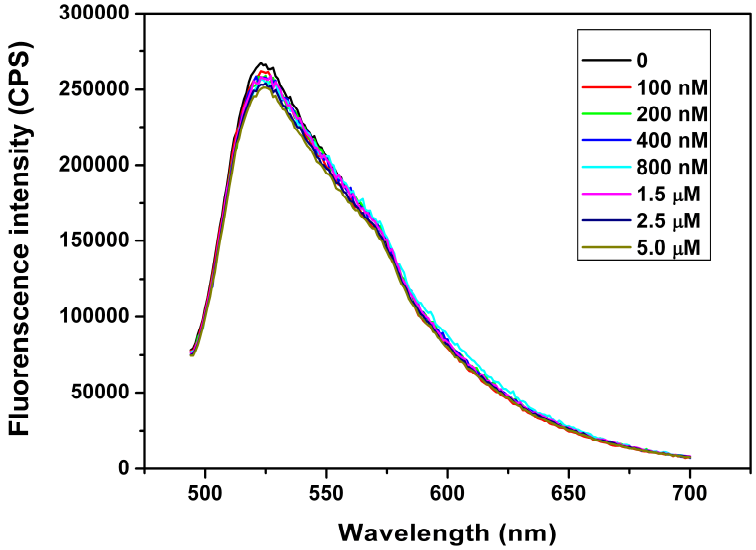

Fig. S2. Fluorescence emission spectra of PG in the presence of different concentrations of Pb^{2+} from 0 to 5.0μM. λ_{ex} = 480 nm.

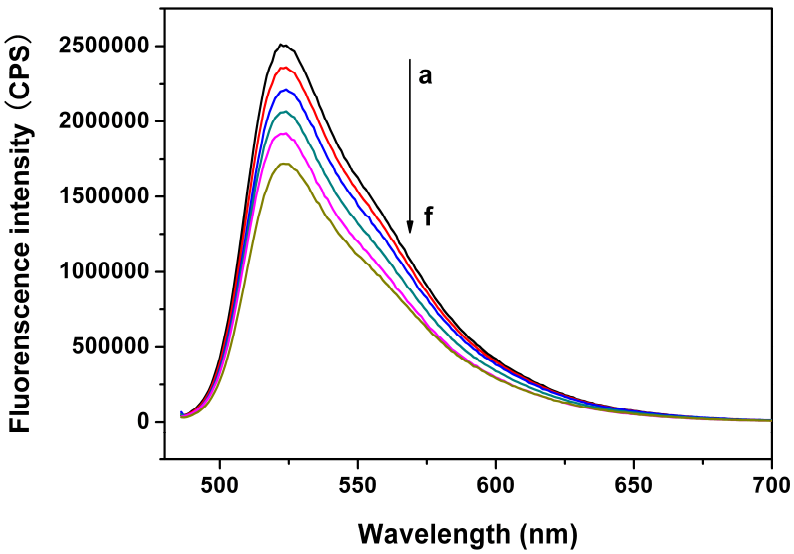

Fig. S3. Application of the DNAzyme sensor to the analysis of soil samples: blank (curve a), soil sample diluted 100 times (curve b), soil sample diluted 50 times (curve c), soil sample diluted 20 times (curve d), soil sample diluted 10 times (curve e), soil sample diluted 5 times (curve f), λ_{ex} = 480 nm.

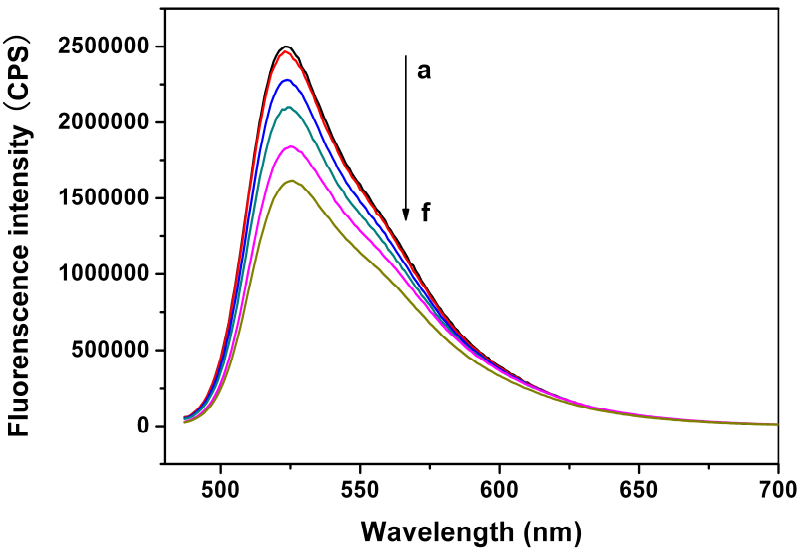

Fig. S4. Application of the DNAzyme sensor to the analysis of Pb^{2+} in fresh water samples: blank (curve a), lake water (curve b), lake water + 20 nM Pb^{2+} (curve c), lake water + 50 nM Pb^{2+} (curve d), lake water + 100 nM Pb^{2+} (curve e), lake water + 200 nM Pb^{2+} (curve f), λ_{ex} = 480 nm.