A supramolecular probe for colorimetric detection of Pb^{2+} based on recognition of G-quadruplex

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Material details

Materials

The G-rich oligonucleotides, PS2.M (GTGGGTAGGGCGGGTTGG), pw17 (GGGTAGGGCGGGTTGGG), T30695 (GGGTGGGTGGGTGGGT), were obtained from Sangon Biotechnology Co., Ltd. (Shanghai, China). The metal salt (KCl, $MgCl_2$, $ZnCl_2$, $FeCl_3$, $CuSO_4$, $CoCl_2$, $MnCl_2$, $Hg(NO_3)_2$, $CdCl_2$, $NiCl_2$), methanol, and Tris (Tris(hydroxymethyl)aminomethane) were all analytical grade, being purchased from Beijing Chemical Company. Pb^{2+} standard solution (1000 μg/mL) was purchased from General Research Institute for Nonferrous Metals of China. The cyanine dye MTC was synthesized according to Hamer and Fichen's methods, and the purity was proved by mass spectrometry and nuclear magnetic resonance (NMR).

Ultrapure water used throughout the experiments was prepared by Milli-Q Gradient ultrapure water system (Millipore). The stock solution of MTC was prepared by dissolving MTC in methanol. The stock solution of G-rich oligonucleotides were prepared by dissolving G-rich oligonucleotides directly into Tris-HCl buffer (10 mM, pH=7.4) and quantified using UV-Vis absorption spectroscopy with the following extinction coefficients ($\varepsilon_{260\ nm}$) for every nucleotide (A=15400, G=11500, C=7400, T=8700). Then the stock solution was stored for more than 24 h at 4℃. Before use, Pb^{2+} standard solution was diluted to required concentration with Tris-HCl buffer.

Spectral measurement

The circular dichroism (CD) spectrum was obtained on a JASCO J-810 circular dichroism spectrometer at room temperature. Spectra were collected with scan speed of 1000 nm• min^{-1}. The spectrum was recorded in the wavelength range of 200-400 nm and has been presented as the average of three successive runs. The spectrum was subtracted from a baseline corresponding to buffer alone.

Ultraviolet (UV) spectra were measured on an Agilent 8453 UV-visible spectrophotometer at the wavelength range 190-1100 nm using a 1 cm path cell at room temperature (25^{o}C). Ultrapure water was used as reference.

Preparation of probe solution

Firstly, MTC was dissolved by using methanol to prepare the mother solution of 200 μM MTC. Secondly, adding the 10 mM Tris-HCl buffer solution containing different concentration of KCl into the MTC solution to prepare MTC aggregates (The volume of the Tris-HCl buffer solution is 10-fold of the MTC mother solution and the portion of methanol in assay solution is 2% in volume.). Then, adding oligonucleotides into solution to change the state of aggregates. Finally, adding different concentration of Pb^{2+} into the system. These mixtures were kept at room temperature for 10 minutes to ensure Pb^{2+} replace K^{+} in the G-quadruplex.

The details of the detection limit calculation

The calculation of the detection limit for Pb^{2+} was according to the 3σ/slope rule, where σ represents the standard deviation of the blank samples, which is about 0.0648 for 3 measurements. The slope is 0.139 according to the inset figure in Fig. 4a. For the X-axis value, 'nM' was used as the unit of [Pb^{2+}].

Application

Lake water was used to confirm the feasibility of the probe for analysis of real-world sample. Lake water was harvested from Peking University, the insoluble matter in which was removed through centrifuge. Certain concentrations of Pb^{2+} were added into the lake water. 10% lake water was titrated into the probe solution to detect the recovery. The probe solution with the Pb^{2+} standard solution and that with the lake samples were measured as the above mentioned method. The absorbance at 580 nm of MTC with the Pb^{2+} standard solution versus [Pb^{2+}] was used to make the standard curve. Then the value of [Pb^{2+}] was obtained based on the absorbance at 580 nm of MTC with the lake samples.

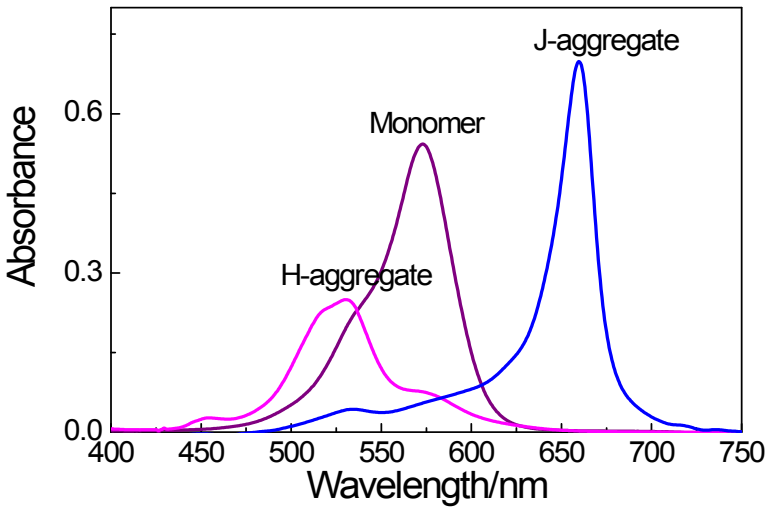

Fig. S1. The absorption spectra of 5 μM MTC in monomer, H-aggregate, and J-aggregate states.

The response of pw17 and T30695 G-quadruplexes to Pb^{2+}

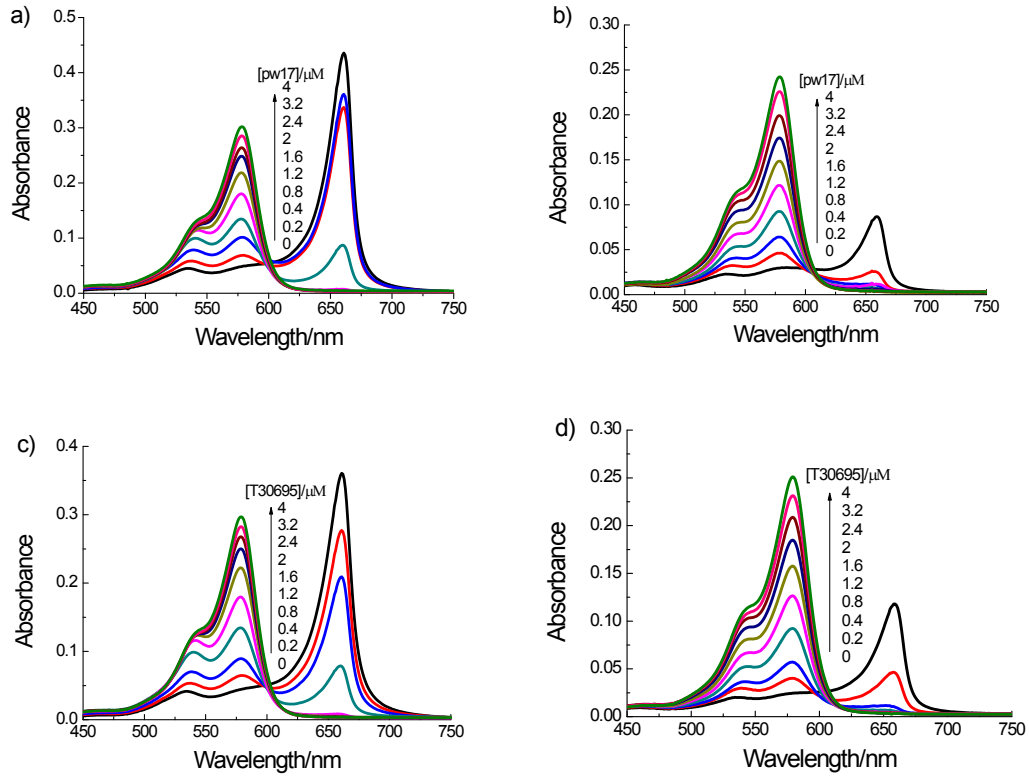

Fig. S2. The absorption spectra of 4 μM MTC with increasing concentrations of variant G-quadruplexes in Tris-HCl buffer solution. a) 10 mM K^+-induced pw17 G-quadruplexes ; b) 40 μM Pb^{2+}-induced pw17 G-quadruplexes in the presence of 10mM K^+ ; c) 10 mM K^+-induced T30695 G-quadruplexes ; d) 40 μM Pb^{2+}-induced T30695 G-quadruplexes in the presence of 10mM K^+.