Visual detection of mercury (II) based on recognition of the G-quadruplex conformational transition by a cyanine dye supramolecule

Hongbo Chen,[a,b] Xiufeng Zhang,*[a] Hongxia Sun,*[b] Xiaoran Sun,[a] Yunhua Shi,[b] Shujuan Xu,[b] and Yalin Tang*[b]

[a]College of Chemistry Engineering, North China University of Science and Technology, Tangshan, 063009, PR China. E-mail: zhangxf@heuu.edu.cn.

[b] National Laboratory for Molecular Sciences, Center for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species. Institute of Chemistry Chinese Academy of Sciences, Beijing, 100190, PR China. E-mail: hongxsun@iccas.ac.cn and tangyl@iccas.ac.cn.

Materials and Methods

Sample Preparation. The cyanine dye MTC was synthesized according to Hamer's[28] and Brooker's[29] methods, and the purity was evaluated by mass spectrometry and nuclear magnetic resonance. The oligonucleotide AS1411 (5'-TTTGGTGGTGGTGGTTGTGGTGGTGGTGG-3') was purchased from Sangon Biotech Co. Ltd. (Shanghai, China), purified by PAGE. The metal salt (KCl, $MgCl_2$, $ZnCl_2$, $FeCl_3$, $CuSO_4$, $CoCl_2$, $MnCl_2$, $Hg(NO_3)_2$, $CdCl_2$, $Pb(NO_3)_2$, $NiCl_2$), Tris (Tris(hydroxymethyl)aminomethane) and 2'6-pyridinedicarboxylic acid (PDCA) were all analytical grade, being purchased from Beijing Chemical Company. Ultrapure water prepared by Milli-Q Gradient ultrapure water system (Millipore) was used throughout the experiments. The stock solutions of the oligonucleotides were prepared by dissolving oligonucleotides directly into 10 mM Tris-HCl buffer solution (pH 7.2). The stock solution of MTC was prepared by dissolving it in methanol to 200μM and then stored in the dark. The concentrations of DNA stock solutions were determined by measuring their absorbance at 260 nm.

Spectroscopy Measurement. 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°C). Ultrapure water was used as reference.

CD spectra were collected from 200 to 350 nm on a Jasco-815 automatic recording spectropolarimeter with a 1cm path-length quartz cell at 25 ºC. Spectra were collected with scan speed of 1000nm/min. Each spectrum was the average of three scans. A solution containing no oligonucleotide was used as reference, and a buffer blank correction was made for all spectra. The cuvette-holding chamber was flushed with a constant stream of dry N_2 gas to avoid water condensation on the cuvette exterior.

The details of 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. 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 10mM KCl into the MTC solution to prepare MTC J-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.). Finally, adding AS1411 induced by different concentration of Hg^{2+} into solution to change the state of aggregates. These mixtures were kept at room temperature for 10 minutes to ensure the J-aggregate change totally.

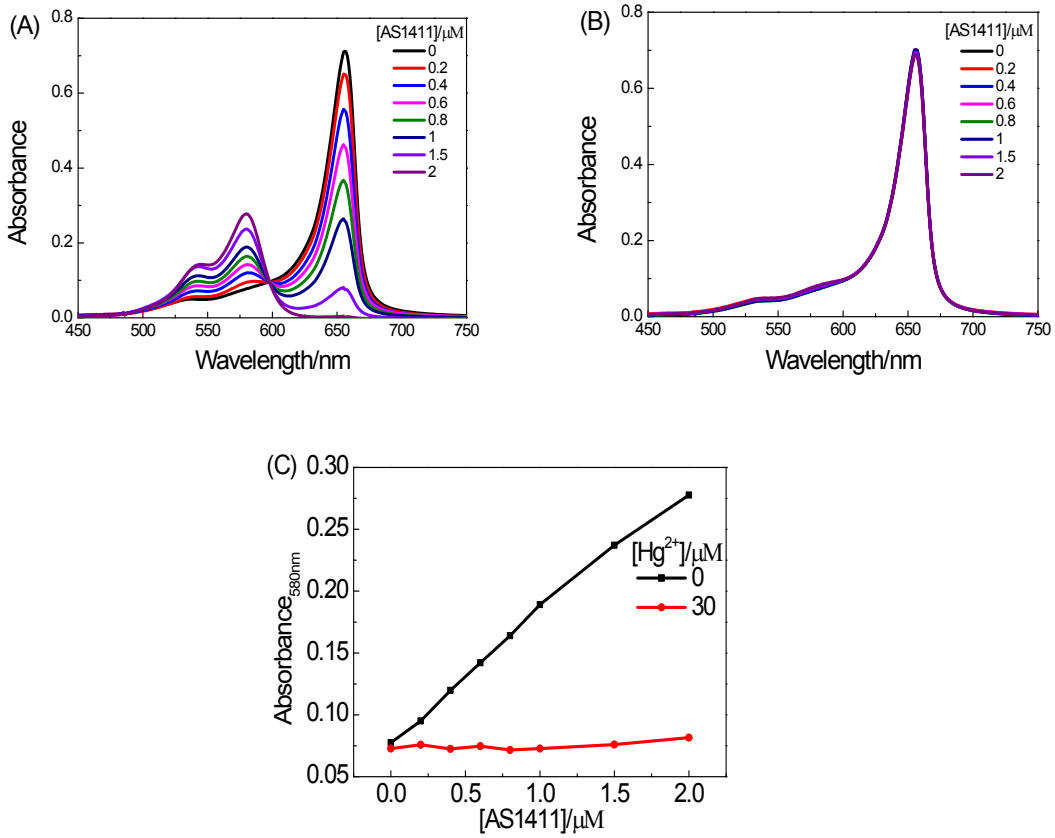

Figure S1. The absorption spectra of 4 μM MTC with increasing AS1411 (A) in the absence of Hg^{2+} and (B) in the presence of 30 μM Hg^{2+}. Experimental conditions: 10 mM Tris-HCl (pH 7.2) containing 10 mM K^{+}. (C) The plots of the absorbance at 580 nm versus [AS1411] in the presence of 30 μM Hg^{2+} or not.

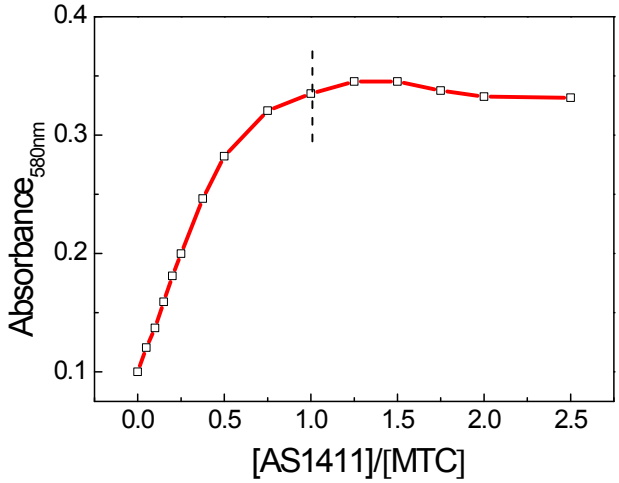

Figure S2. The absorbance of 4 μM MTC at 580 nm with different ratio of [AS1411]: [MTC]. Experimental conditions: 10 mM Tris-HCl (pH 7.2) containing 10 mM K^+.

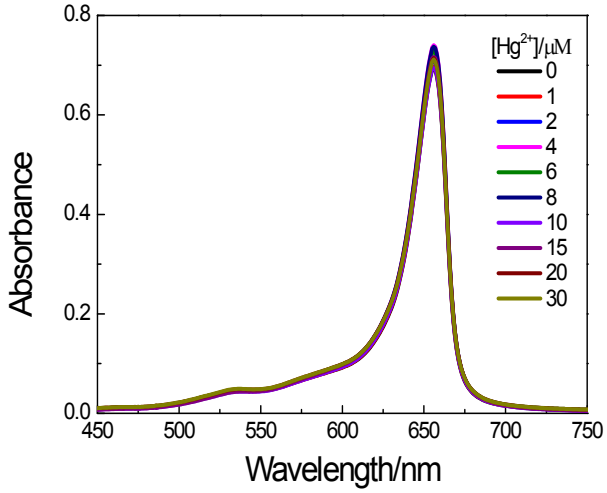

Figure S3. The absorption spectra of 4 μM MTC with increasing Hg^{2+}. Experimental conditions: 10 mM Tris-HCl (pH 7.2) containing 10 mM K^+.

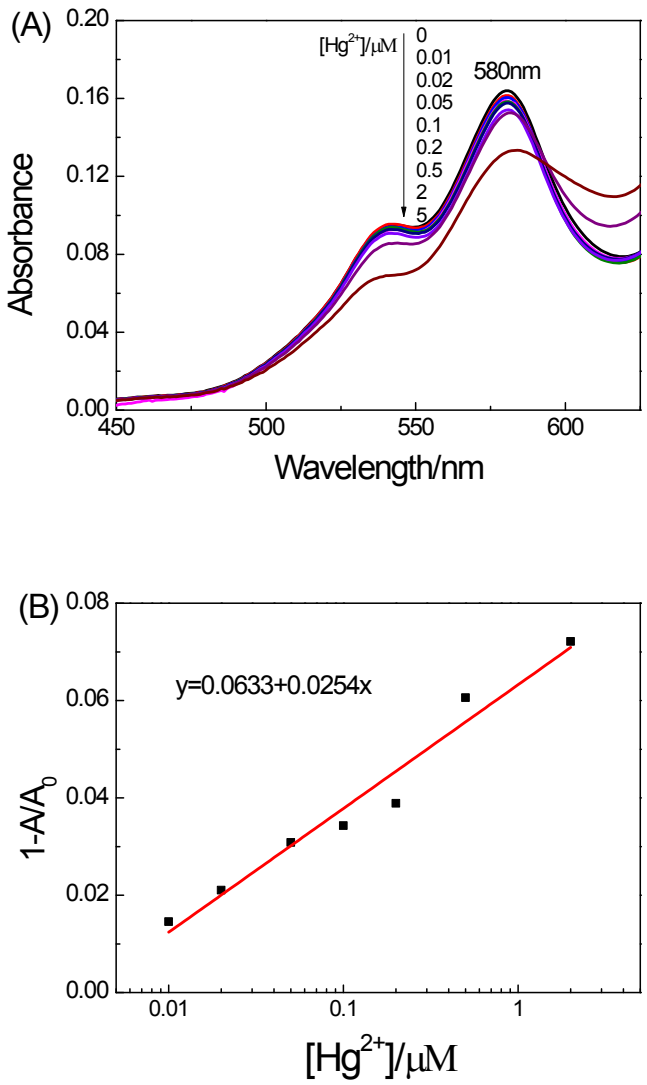

Figure S4. (A) The absorption spectra of 0.5μM AS1411 and 4 μM MTC in 10mM Tris-HCl with 10 mM K^+ (pH 7.2) to analyze different concentrations of Hg^{2+}. (B) The linear correlation of the absorbance change with logarithmic concentrations of Hg^{2+} within the range of 10 nm to 2 μM (A_0 and A stand for the absorbance at 580 nm in the absence and presence of Hg^{2+}).