Electronic Supplementary Information

Construction of DNA logic gates utilizing an H^+/Ag^+ induced i-motif structure

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Materials and methods

Sample preparation

The cyanine dye DMSB was synthesized according to Brooker's[1] and Hamer's[2] methods, and the purity was evaluated by mass spectrometry and nuclear magnetic resonance. The oligonucleotide（AS1411） was purchased from Sangon Biotech Co., Ltd. (Shanghai, China), purified by PAGE. Analytical grade methanol, NaH_2PO_4, Na_2HPO_4 and ethylenediaminetetraacetic acid (EDTA) were purchased from Beijing Chem. Co. (China 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 PBS (pH 7.4).

The stock solution of DMSB was prepared by dissolving it in methanol to 200mM and then storing in the dark at -4 ºC. The stock solutions of oligonucleotides were prepared by dissolving them to phosphate buffer (10mM Na_2HPO_4/ NaH_2PO_4, 1mM EDTA, pH 7.4) followed by filtering through a microfiltration membrane (Φ=0.22 μm). Then they were heated to 90 ºC for 5 min and gradually cooled to room temperature at a rate of 1 ºC min^{-1}. The concentrations of DNA stock solutions were determined by measuring their absorbance at 260 nm. All DNA samples were stored for more than 24 h at -4 ºC and then structurally identified by circular dichroism (CD) spectra.

Spectroscopy measurement

Fluorescence spectra were taken on a Hitachi F-4500 spectrophotometer in a 10 mm quartz cell at room temperature. Xenon arc lamp was used in the excitation light source in fluorescence measurement. The excitation wavelength was 520 nm. Both excitation and emission slits were 10 nm and the voltage was 700 V with a scan speed of 1200 nm/min.

Circular dichroism (CD) spectra were collected from 200 to 350 nm on a Jasco-815 automatic recording spectropolarimeter with a 1-cm path-length quartz cell at 25 ºC. Spectra were collected with scan speed of 500nm/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 temperature of the cell holder was regulated by a JASCO PTC-423S temperature controller. The cuvette-holding chamber was flushed with a constant stream of dry N_2 gas to avoid

water condensation on the cuvette exterior.

Table S1 Sequence of all tested oligonucleotides

Name	sequence
cAS1411	5'-CCACCACCACCACAACCACCACCACCAAA-3'
TBA	5'-CCAACCACACCAACCAAA-3'
C-Kit	5'-CCCTCCCTCGCGCCCGCCCGAAA-3'
HIF-1α	5'-CCCGCCCCCTCTCCCTCCCAAA-3'
VEGF	5'-CCCGCCCCCGGCCCGCCCAAA-3'
Telomere	5'-CCCTAACCCTAACCCTAACCCT-3'
Bcl-2	5'-CCCGCCCAATTCCTCCCGCGCCC-3'
C-myc	5'-CCTTCCCCACCCTCCCCACCCTCCCCA-3'

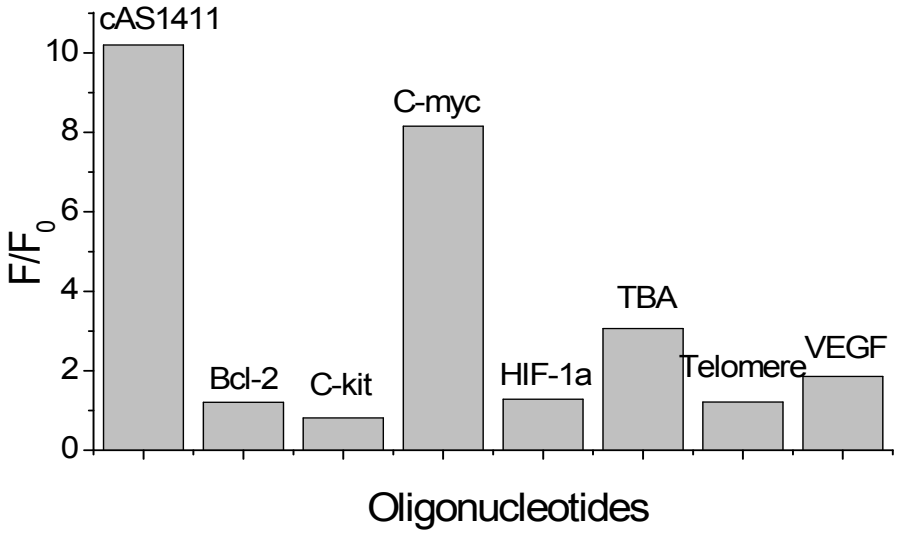

Fig. S1 The fluorescence intensity ratio of F/F_0 of 5 μM DMSB at 580 nm with 2μM various oligonucleotides present in PB buffer solution. F_0 and F are the fluorescence intensities of 5μM DMSB in the presence of the oligonucleotides with a single-stranded and an i-motif conformation, respectively.

All the eight sequences tend to form i-motif at acidic conditions, and keep single-stranded conformation under neutral or alkaline conditions. Fig. S1 shows the fluorescence intensity of DMSB with i-motif divides by that with single-stranded DNA for each oligonucleotide. It is obvious that the fluorescence of DMSB shows the most dramatic enhancement with cAS1411 i-motif.

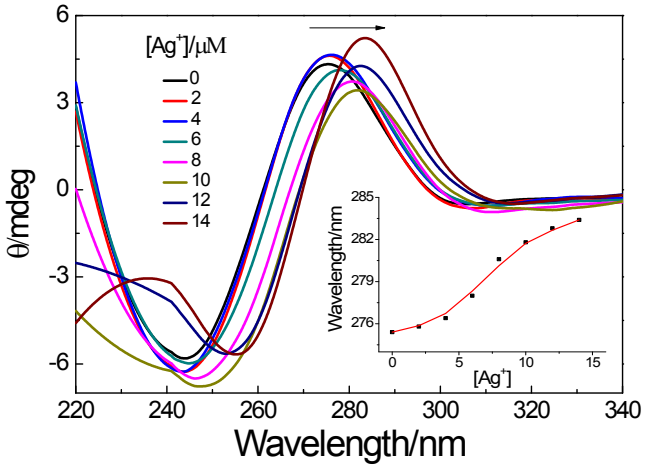

Fig. S2 The CD spectra of 2 μM cAS1411 with increasing concentrations of Ag^+ in the presence of 5μM DMSB in PB solution. The positive band has obvious red shift from 272nm to 284nm, which indicated that the cytosine-rich single stand DNA gradually formed i-motif structure with the addition of an increasing concentration of Ag^+ in the presence of 5μM DMSB in PBS.

Fig. S2 shows that the positive band has obvious red shift from 272nm to 284nm with an increasing amount of Ag^+, corresponding to the CD feature of i-motif,[3,4] indicating that the cytosine-rich single-stranded DNA gradually formed i-motif structure.

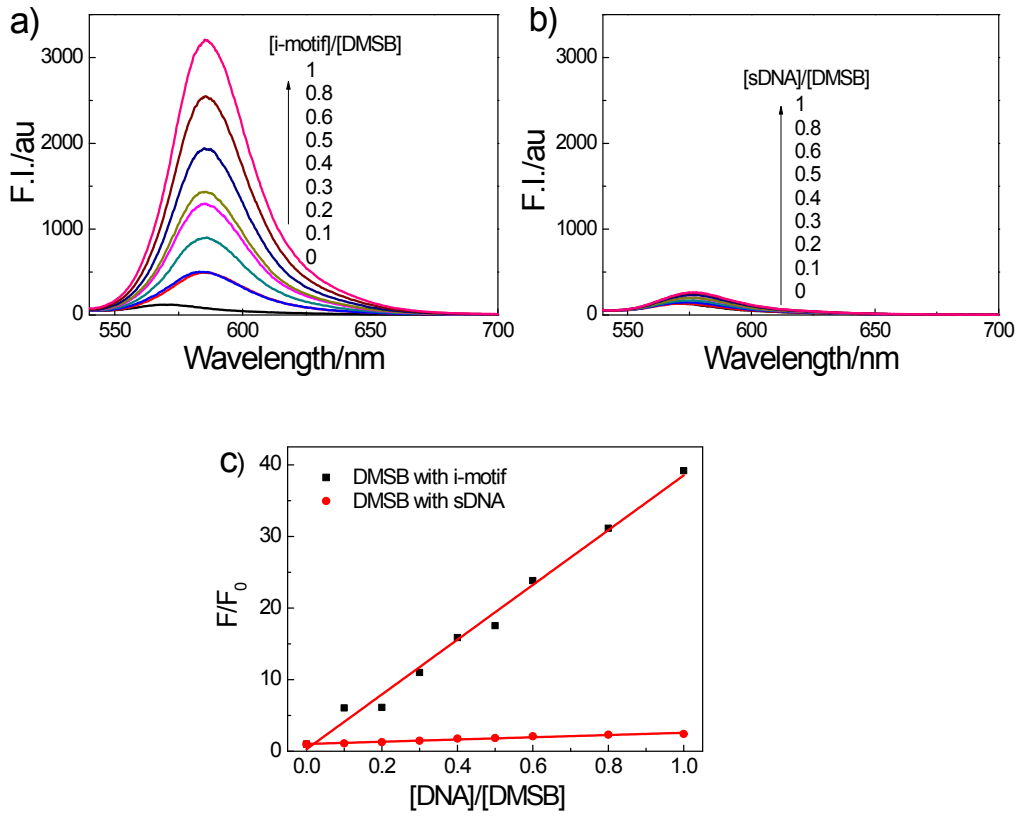

Fig. S3 The fluorescence of 5 μM DMSB with increasing concentrations of i-motif a) and b) single-stranded DNA in PBS. c) Comparison of the fluorescence intensity of DMSB interact with different DNA structures (black squares: i-motif; red dots: single-stranded DNA) in PBS. Both i-motif and single-stranded DNA are formed by cAS1411.

DMSB showed an obvious enhancement of fluorescence when interacting with i-motif (Fig. S3). This phenomenon did not appear when DMSB interacted with single-stranded DNA (Fig. S3). This result indicates the property of DMSB to recognize i-motif formation.

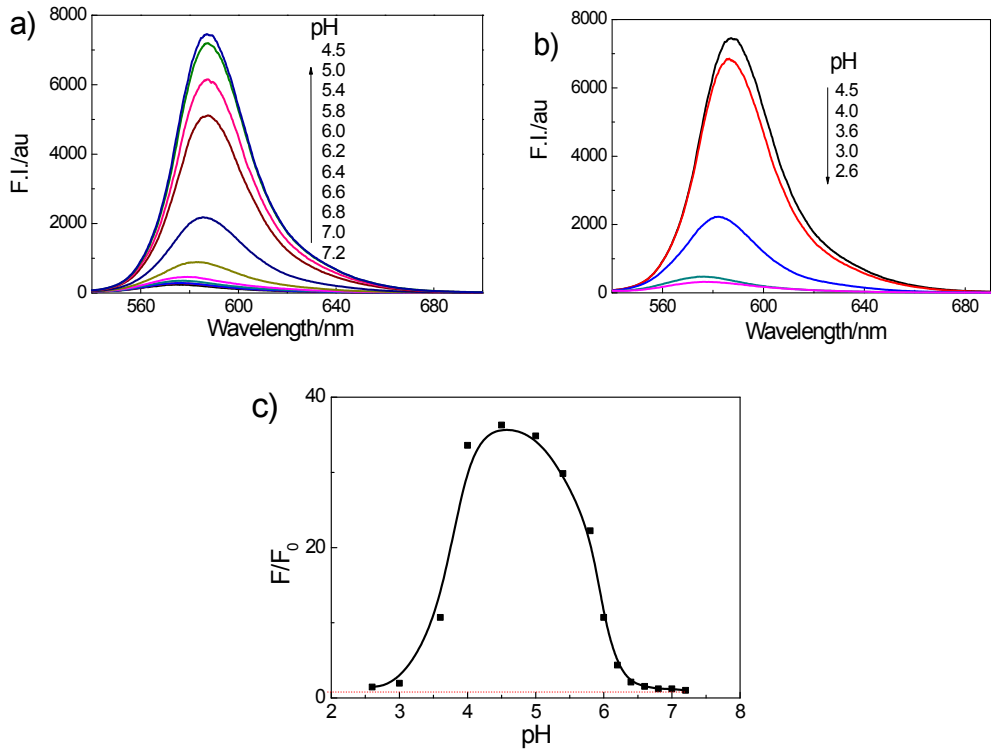

Fig. S4 a) and b) The fluorescence spectra of 5 μM DMSB with variant pH in the presence of 2 μM cAS1411 DNA in PB solution. c) The plot of the fluorescence intensity at 580 nm versus pH.

DMSB exhibited a dramatic enhancement of fluorescence intensity within the pH from 7.2 to 4.5 and then a sharp decrease within the range of 4.5 to 2.6. Despite of decrease, the fluorescence intensity at pH 3 is still higher than that at pH 7.2, meaning the system still can be used at pH 3.

References

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