Electronic Supplementary Information

Reversible regulation of the supramolecular chirality of a cyanine dye by using G-quadruplex structure as a template

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Materials and methods

Sample preparation

The cyanine dye MTC was synthesized according to Brooker's methods[1,2], and the purity was evaluated by mass spectrometry and nuclear magnetic resonance. The oligonucleotide ONS was purchased from Invitrogen (Beijing, China), purified by PAGE. Analytical grade methanol, NaH_2PO_4, Na_2HPO_4, ethylenediaminetetraacetic acid (EDTA), and ultrapure water prepared by Milli-Q Gradient ultrapure water system (Millipore) were used throughout the experiments. The stock solutions of the oligonucleotides were prepared by dissolving oligonucleotides directly into 10 mM PBS (pH 7.2).

The stock solution of MTC was prepared by dissolving it in methanol to 200 μM and then storing in the dark. The stock solutions of oligonucleotides were prepared by dissolving them to phosphate buffer (20mM Na_2HPO_4/ NaH_2PO_4, 1mM EDTA, pH 7.2), heated to 90 ºC for 5 min, and then 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 12 h at -4 ºC and then structurally identified by circular dichroism (CD) spectra.

Spectroscopy measurement

The UV-vis absorption spectra were measured by an Agilent-8453 UV/visible spectrophotometer equipped with a Peltier effect cuvette holder in 10 mm quartz cells.

CD spectra were collected from 200 to 800 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 obtained on 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.

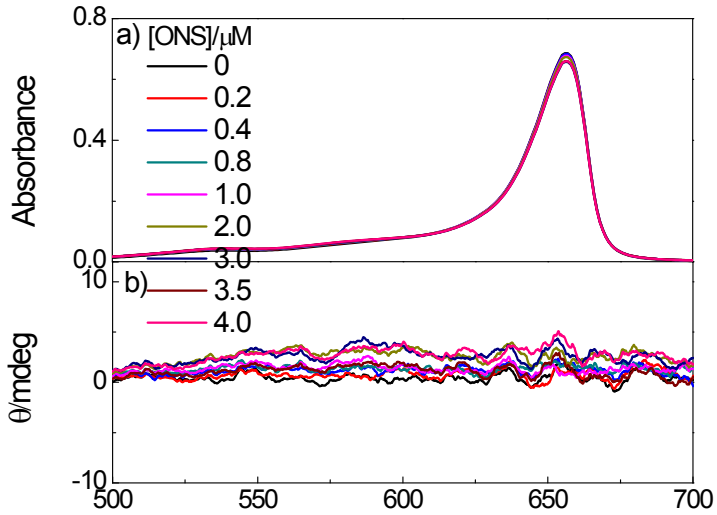

Fig. S1. The UV (a)and CD (b) spectra of 4 μM MTC with the increasing concentrations of ONS in PB solution (20mM Na_2HPO_4/NaH_2PO_4, 1mM EDTA , pH 7.2).

MTC mainly exhibits J-aggregate state and ONS exists in duplex in PBS without Ag^+. When ONS is added into the MTC solution, MTC still exhibits a predominant absorption band assigned to J-aggregate and little change is observed with the increasing concentrations of ONS. Meanwhile, no peak appears in the CD spectra of MTC. That means ONS duplex has no effect on the assembly of MTC.

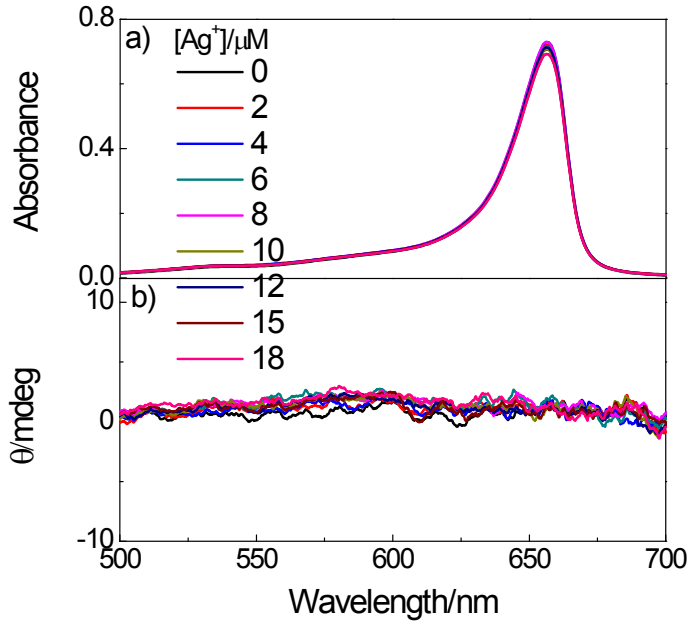

Fig. S2. The UV (a) and CD(b) spectra of 4 μM MTC with the increasing concentrations of Ag^+ in PB solution (20 mM Na_2HPO_4/NaH_2PO_4, 1 mM EDTA , pH 7.2).

In Fig. S2, the UV and CD spectra of MTC show no change with the increasing concentrations of Ag^+ in PB solution without ONS present, meaning Ag^+ has no effect on the chirality of MTC.

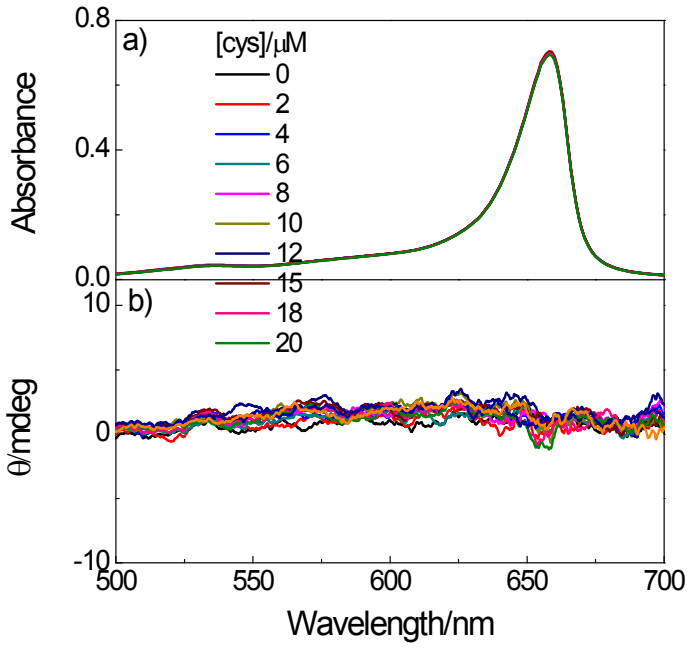

Fig. S3. The UV (a) and CD (b) spectra of the 4 μM MTC with the increasing concentrations of Cys in the presence of 15μM Ag^+ in PB solution (20mM Na_2HPO_4/NaH_2PO_4, 1mM EDTA, pH 7.2).

As displayed in Fig. S3, without ONS, the MTC exhibits no change in its UV and CD spectra with increasing concentrations of Cys, meaning Cys has no effect on the chirality of MTC.

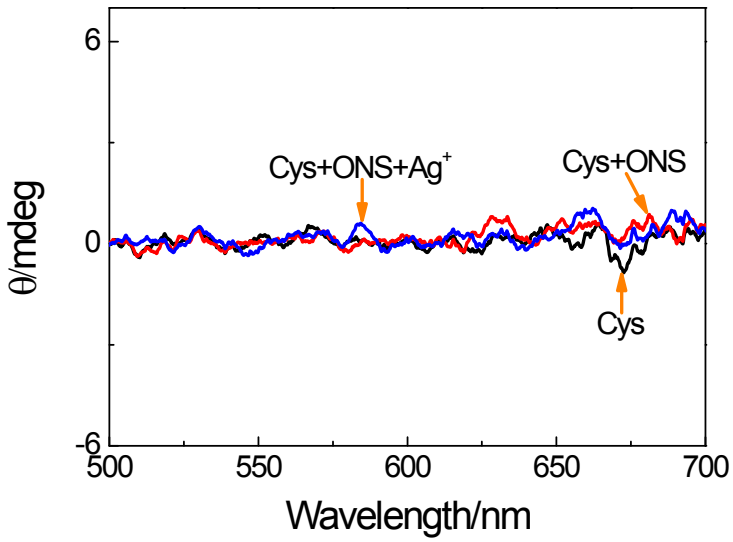

Fig. S4. The CD spectra of Cys, Cys with ONS, Cys with ONS and Ag^+, and in PB solution (20 mM Na_2HPO_4/ NaH_2PO_4, 1 mM EDTA, pH 7.2). The concentration of Cys, ONS, and Ag^+ is 15 μM, 2 μM, 15 μM, respectively.

The Cys has no characteristic CD signal between 500 nm and 700 nm in the system, which means the CD spectra of Cys has no effect on the CD spectra of MTC.

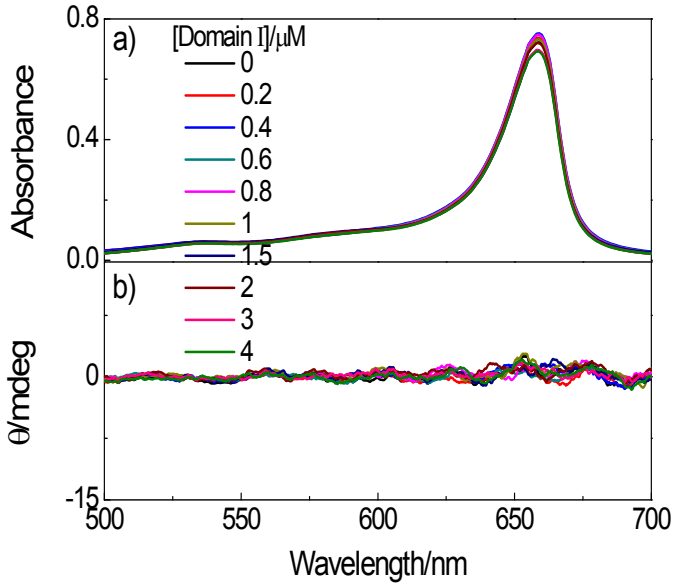

Fig. S5. The UV (a) and CD (b) spectra of 4 μM MTC with the increasing concentrations of Domain I (GGGTACGCTCTTCAAAAGAAGACCCTACCC) in the presence of 15μM Ag^+ in PB solution (20mM Na_2HPO_4/NaH_2PO_4, 1mM EDTA , pH 7.2).

Domain I forms duplex structure in the presence of 15μM Ag^+ in PB solution. With increasing amounts of Domain I, MTC shows no change in its UV and CD spectra, meaning cannot cause any change of the MTC aggregates in PB solution.

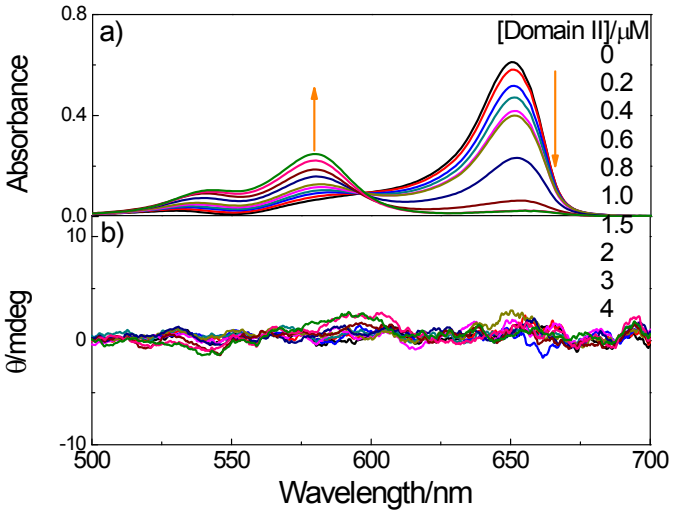

Fig. S6. The UV (a) and CD (b) spectra of 4 μM MTC with the increasing concentrations of Domain II (AGGGTTGGGCGGGATGGG) in the presence of 15μM Ag^+ in PB solution (20mM Na_2HPO_4/NaH_2PO_4, 1mM EDTA, pH 7.2).

Domain II forms G-quadruplex structure in the presence of 15μM Ag^+ in PB solution. With increasing amounts of Domain II, the absorbance at 656 nm decreases while the absorbance at 578 nm increases, corresponding to the transition of MTC from J-aggregate to monomer. In the CD spectra of MTC, no signal appears, meaning no chirality is induced.

References

1. Brooker LGS. The Cyanine Dyes and Related Compounds. *Journal of the American Chemical Society* 1965, 87: 937-938.

2. Brooker LGS, White FL. Studies in the Cyanine Dye Series. I. A New Method of Preparing Certain Carbocyanines. *Journal of the American Chemical Society* 1935, 57: 547-551.