A Colorimetric and Fluorometric Dual-Modal Supramolecular Chemosensor and Its Application for HSA Detection

Hongxia Sun,[a,b] Junfeng Xiang,[a] Xiufeng Zhang,[c] Hongbo Chen,[c] Qianfan Yang,[a] Qian Li,[a]
Aijiao Guan,[a] Qian Shang,[a] Yalin Tang[a] and Guangzhi Xu[a]

[a] 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, Zhongguancun North 1st street 2, Beijing 100190, P. R. China. E-mail: tangyl@iccas.ac.cn
[b] University of the Chinese Academy of Sciences, Yuquan Road 19(A), Shijingshan District, Beijing 100049, P. R. China.
[c] College of Chemistry Engineering, Hebei United University, Tangshan, Hebei, 063009, P. R. China.
Experimental Section

Probe solution preparation

MTC was first dissolved by using methanol to prepare the mother solution of 200 μM MTC. Added the 10 mM Tris-HCl buffer solution containing 1M NaCl into the MTC solution to prepare MTC H₂-aggregate (the volume of the Tris-HCl buffer solution is 2-fold of the MTC mother solution), and then 10 mM Tris-HCl buffer solution was further added to dilute the MTC H₂-aggregate as well as Na⁺ to a final concentration. MTC J-aggregate was prepared by directly adding 10 mM Tris-HCl buffer solution with a specific concentration of NaCl into the MTC mother solution. MTC H₁-aggregate was prepared by directly adding 10 mM Tris-HCl buffer solution without metal ions into the MTC mother solution.

Spectroscopy measurement

Ultraviolet (UV) spectra were measured on a Agilent 8453 UV-visible spectrophotometer at the wavelength range 200～1000 nm using a 1 cm path cell at room temperature. Ultrapure water was used as reference. Fluorescence spectra were recorded on a Hitachi F4500 spectrofluorometer (Japan) in a 1-cm x 0.2-mm path-length quartz cell at room temperature. Xenon arc lamp was used as the excitation light source. The excitation and emission slits were both 10 nm. Excitation was set at 570 nm, and emission was collected from 580 to 720 nm. The scan speed was 240 nm/min.

HSA in urine detection

Urine was used to confirm the feasibility of this aptasensor for analysis of real-world sample. Urine samples were harvested from a healthy person. HSA was added into the urine samples to mimic the urine samples with 0, 20, 100, 200, and 400 mg/L HSA. Added 2 mL ethanol into 1mL urine samples to precipitate protein. After removed the supernatant, 1mL probe solution containing 3μM MTC and 8 mM NaCl was titrated in. Then the probe solution was then photographed by a camera.
**Fig. S1** The curves of the monomeric MTC absorbance at 602 nm against [HSA]. The error bars mean standard deviation (n=3 (number of measurements)).
**Fig. S2** The absorption spectra of a) 10 μM, b) 7.5 μM, c) 5 μM and d) 2.5 μM MTC in H₂-aggregate state with increasing [HSA] in 10 mM Tris-HCl buffer solution (pH 7.2) with 8 mM NaCl. e) The curves of the absorbance ratio $A_{602\text{nm}}/A_{450\text{nm}}$ against [HSA], and the error bars mean standard deviation (n=3 (number of measurements)). f) The photos of the MTC probe solution with increasing amounts of HSA.
**Fig. S3** The absorption spectra of a) 10 μM, b) 7.5 μM, c) 5 μM and d) 2.5 μM MTC in J-aggregate state with increasing [HSA] in 10 mM Tris-HCl buffer solution (pH 7.2) with 8 mM NaCl. e) The curves of the absorbance ratio $A_{602\text{nm}}/A_{656\text{nm}}$ against [HSA], and the error bars mean standard deviation (n=3 (number of measurements)). f) The photos of the MTC probe solution with increasing amounts of HSA.
Fig. S4 The absorption spectra of 3 μM MTC in H₂-aggregate state with increasing [HSA] in 10 mM Tris-HCl buffer solution (pH 7.2) with a) 120 mM, b) 80 mM, c) 40 mM, and d) 8 mM NaCl. e) The curves of the absorbance ratio $A_{602\text{nm}}/A_{450\text{nm}}$ against [HSA], and the error bars mean standard deviation (n=3 (number of measurements)). f) The photos of the MTC probe solution with increasing amounts of HSA.
**Fig. S5** The absorption spectra of 3 μM MTC in J-aggregate state with increasing [HSA] in 10 mM Tris-HCl buffer solution (pH 7.2) with a) 120 mM, b) 80 mM, c) 40 mM, and d) 8 mM NaCl. e) The curves of the absorbance ratio $A_{602\text{ nm}}/A_{656\text{ nm}}$ against [HSA], and the error bars mean standard deviation (n=3 (number of measurements)). f) The photos of the MTC probe solution with increasing amounts of HSA.