Supporting Information

Rational construction of a triple emission molecular imprinting sensor for accurate naked-eye readout of folic acid

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Contents

1. Related descriptions

Synthesis of SiO_2 nanoparticles

50 mL of ultrapure water, 30 mL of ethanol and 10 mL of $NH_3 \cdot H_2O$ were well mixed in a 250 mL round-bottom flask under stirring. Then, a mixture containing 5 mL of TEOS and 20 mL of ethanol was added dropwise with the help of a constant-pressure dropping funnel. After stirring overnight, the SiO_2 nanoparticles were collected by centrifugation, and washed with ethanol and water for three times, respectively. Finally, the SiO_2 nanoparticles were dispersed in ultrapure water (approximately 10 mg/mL) for further use. (**Materials and regents.** Ethanol and ammonium hydroxide ($NH_3 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Tetraethyloxysilane (TEOS) was obtained from Aladdin (Shanghai, China).)

Synthesis of g-QDs and r-QDs

For GSH-modified g-QDs synthesis, 68.4 mg of $CdCl_2 \cdot 2.5H_2O$ and 0.182 g of GSH were dissolved in 75 mL of ultrapure water and the pH adjusted to 9.0 rapidly. After deoxygenated by bubbling N_2 for 30 min under stirring, 1 mL of the freshly prepared NaHTe aqueous solution (with 40 mg of $NaBH_4$ and 38.3 mg of tellurium powder reacting in 2 mL of ethanol-water mixture (3:1, v/v) at 40℃ for 4 h) was immediately injected into the above reaction system in an N_2 atmosphere. The mixture solution was heated and refluxed for approximately 1 h to obtain g-QDs (emission: 540 nm). The MPA-modified r-QDs emitted at 650 nm was synthesized following the same way, but replacing GSH with 78.5 μL of MPA and prolonging the reflux time to about 32 h. (**Materials and regents.** Glutathione (GSH) was offered by Solarbio (Beijing, China). Cadmium chloride hemi(pentahydrate) ($CdCI_2 \cdot 2.5H_2O$) and 3-mercaptopropionic acid (MPA) were offered by Aladdin (Shanghai, China). Sodium borohydride ($NaBH_4$) and tellurium powder were provided by Sigma-Aldrich (Shanghai, China).)

Pretreatment procedures for milk powder and folic acid tablets

For milk powder pretreatment, 1.0 g milk powder was dissolved in 7 mL of methanol (containing 1 mL of 0.1 M sodium carbonate), followed by adding 1 mL of EDTA (0.1M). After stirring for 60 min, the sample was centrifuged at 5724 g for 15 min and the precipitate was rinsed with 2 mL of methanol again. The two supernatants were mixed and evaporated to dryness under nitrogen stream, redissolving in 1 mL of ultrapure water. For folic acid tablets pretreatment, six tablets were ground to a good powder, and then 0.3 g of powder was accurately weighed and dissolved in 10 mL of NaOH ethanol solution (0.01 M NaOH, 20% ethanol (volume fraction)) by ultrasonic. After centrifugation, the supernatant was diluted to 100 mL by ultrapure water. (**Materials and regents.** Methanol, ethanol and sodium hydroxide (NaOH) were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Sodium carbonate and EDTA were bought from XiLong Chemical (Guangdong, China).

2. Table

Table S1 The related parameter values for the fitting curves in Fig. 4

	$(I_{644}*I_{540}/I_{465})/(I_{644}*I_{540}/I_{465})_0$, in Fig. 4A	$(I_{540}/I_{465})/(I_{540}/I_{465})_0$, in Fig. 4C	$(I_{644}/I_{465})/(I_{644}/I_{465})_0$, in Fig. 4D
model	logistic		
equation	$y=A_2+(A_1-A_2)/(1+(x/x_0)^p)$		
A_1	0.98049 ± 0.00982	0.99874 ± 0.02003	0.97056 ± 0.008
A_2	0.01303 ± 0.00828	-0.00289 ± 0.01181	0.39153 ± 0.01546
x_0	0.68252 ± 0.0315	0.19982 ± 0.01914	2.18336 ± 0.22805
p	1.11352 ± 0.06404	0.85582 ± 0.05953	0.9296 ±0.07371
reduced Chi-Sqr	2.02E-04	5.14E-04	1.63E-04
R^2 (COD)	0.99913	0.99739	0.99788
adjusted R^2	0.99884	0.99652	0.99718

3. Figures

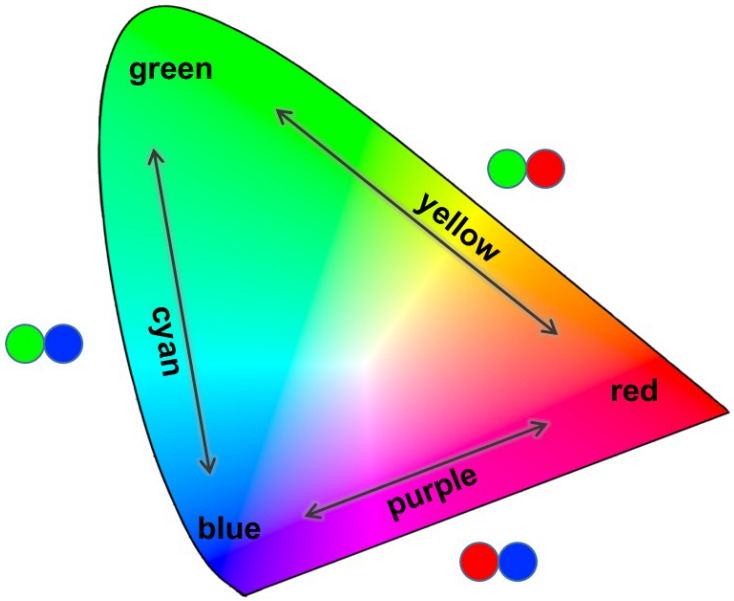
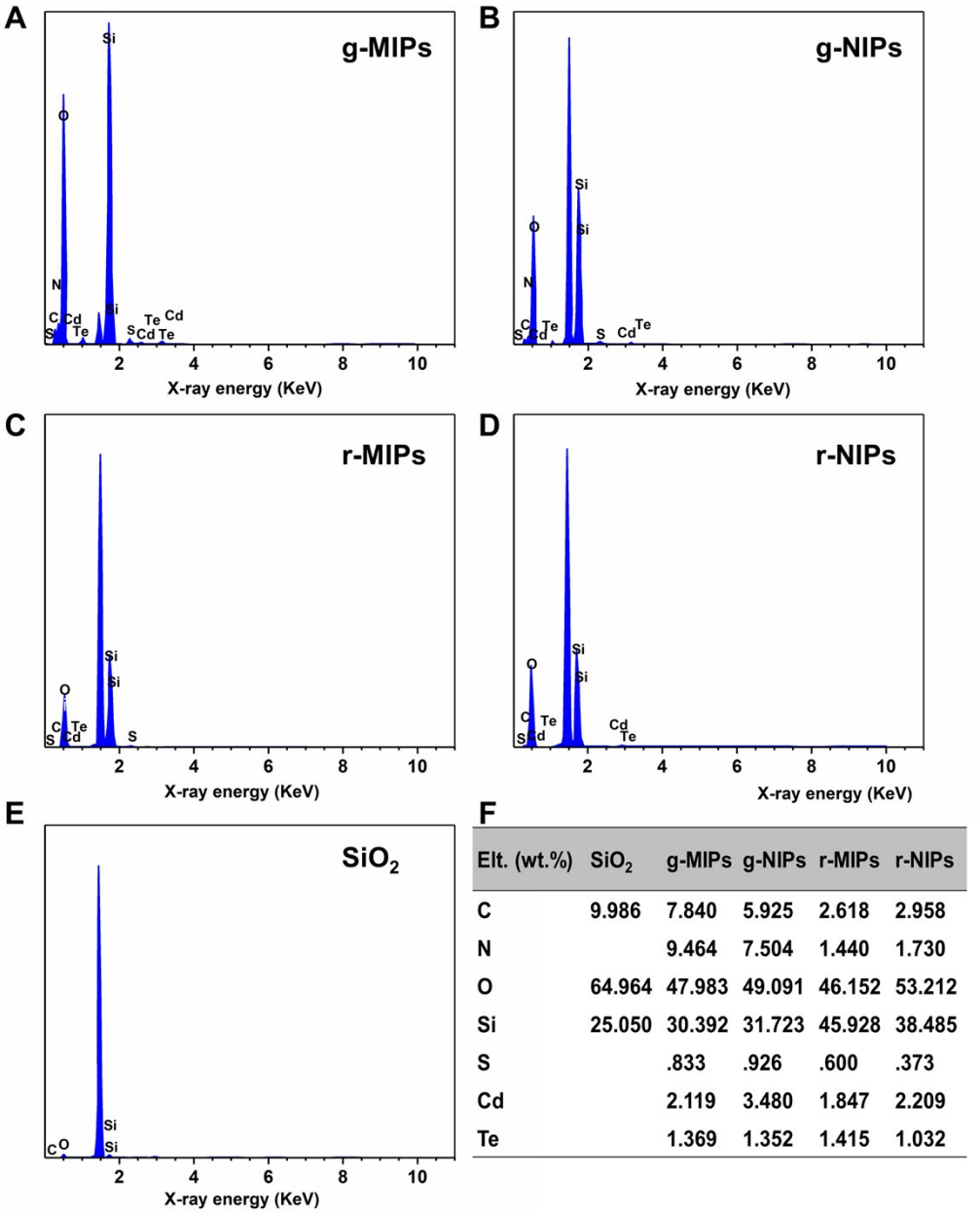


Fig. S1 Chromaticity diagram to indicate the color variation range of dual-emission fluorescence based MIPs sensors with color composite pattern of blue mixed red, blue mixed green, or green mixed red.



F

Elt. (wt.%)	SiO_2	g-MIPs	g-NIPs	r-MIPs	r-NIPs
C	9.986	7.840	5.925	2.618	2.958
N		9.464	7.504	1.440	1.730
O	64.964	47.983	49.091	46.152	53.212
Si	25.050	30.392	31.723	45.928	38.485
S		.833	.926	.600	.373
Cd		2.119	3.480	1.847	2.209
Te		1.369	1.352	1.415	1.032

Fig. S2 EDS spectra of (A) g-MIPs, (B) g-NIPs, (C) r-MIPs, (D) r-NIP and (E) SiO_2 nanoparticles, and (F) the corresponding element contents.

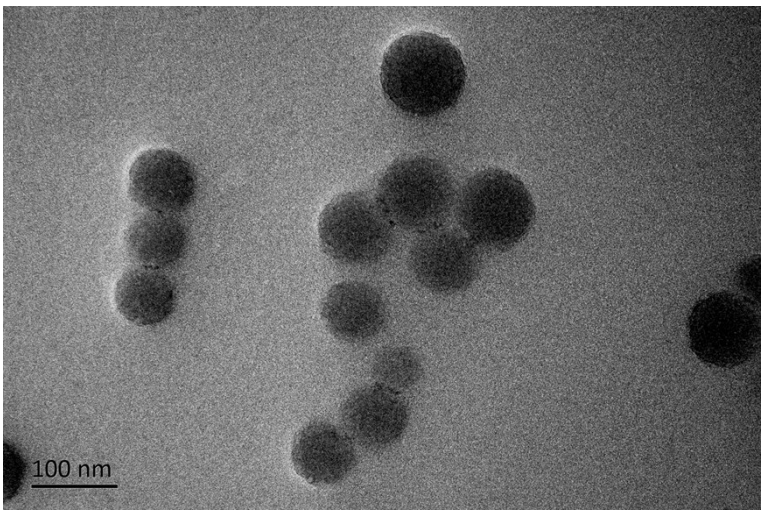


Fig. S3 TEM image of SiO_2 nanoparticles with average dimer of approximately 75 nm.

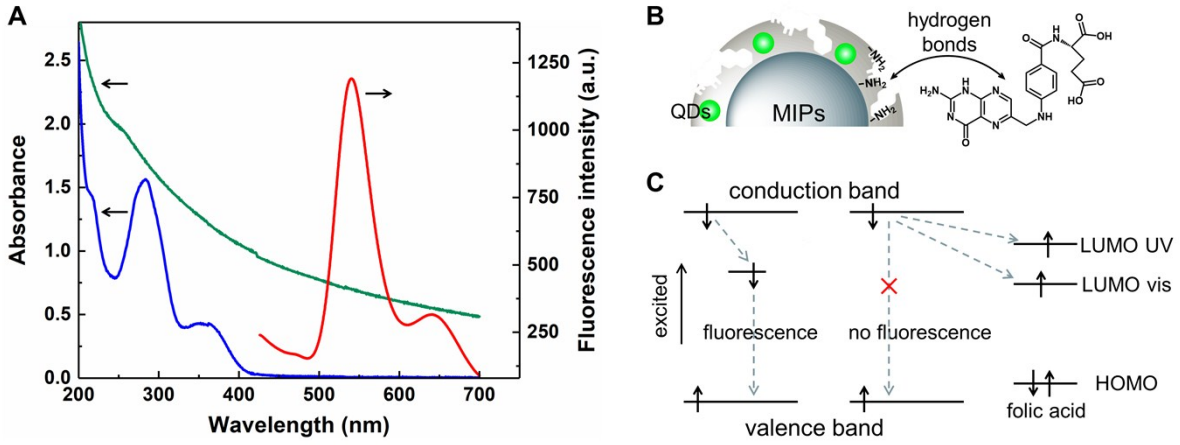


Fig. S4 (A) Absorption spectra of folic acid (blue line) and MIPs sensor (green line), and fluorescence emission spectrum of MIPs sensor (*i.e.*, mixture of g-MIPs and r-MIPs, red line), (B) rebinding behavior diagram between MIPs and target folic acid, and (C) molecular orbital theory for PET process between QDs and folic acid.

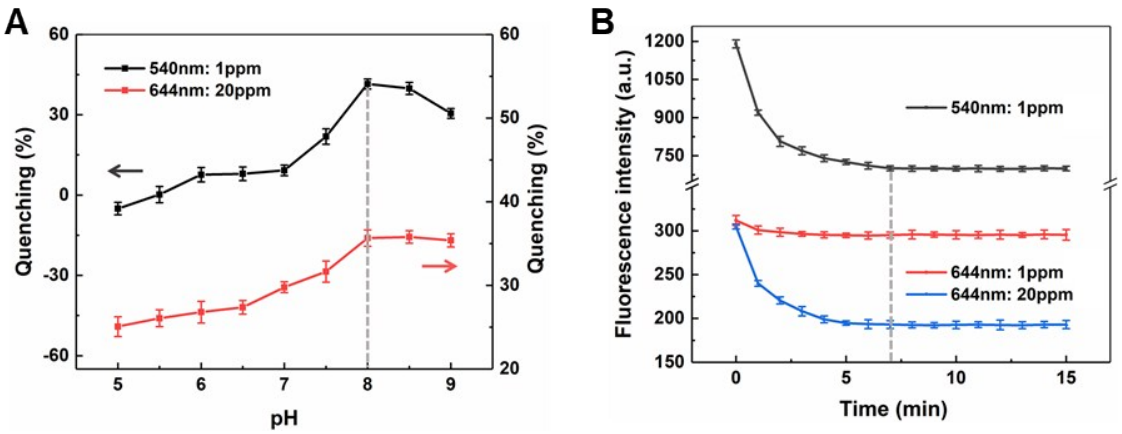


Fig. S5 (A) Quenching degree (*i.e.*, $(I_0\text{-}I)/I_0$) of green-emission peak after the addition of 1 ppm folic acid (black line) and red-mission peak after the addition of 20 ppm folic acid (red line) under different pH conditions; and (B) fluorescence intensity of green-emission peak after the addition of 1 ppm folic acid (black line) and red-emission peak after the 1 ppm folic acid (red line) and 20 ppm folic acid (blue line) with reaction time, respectively. The green-emission peak was located at 540 nm and the red-emission peak was located at 644 nm. I_0 and I mean the fluorescence intensity before and after the addition of folic acid, respectively.

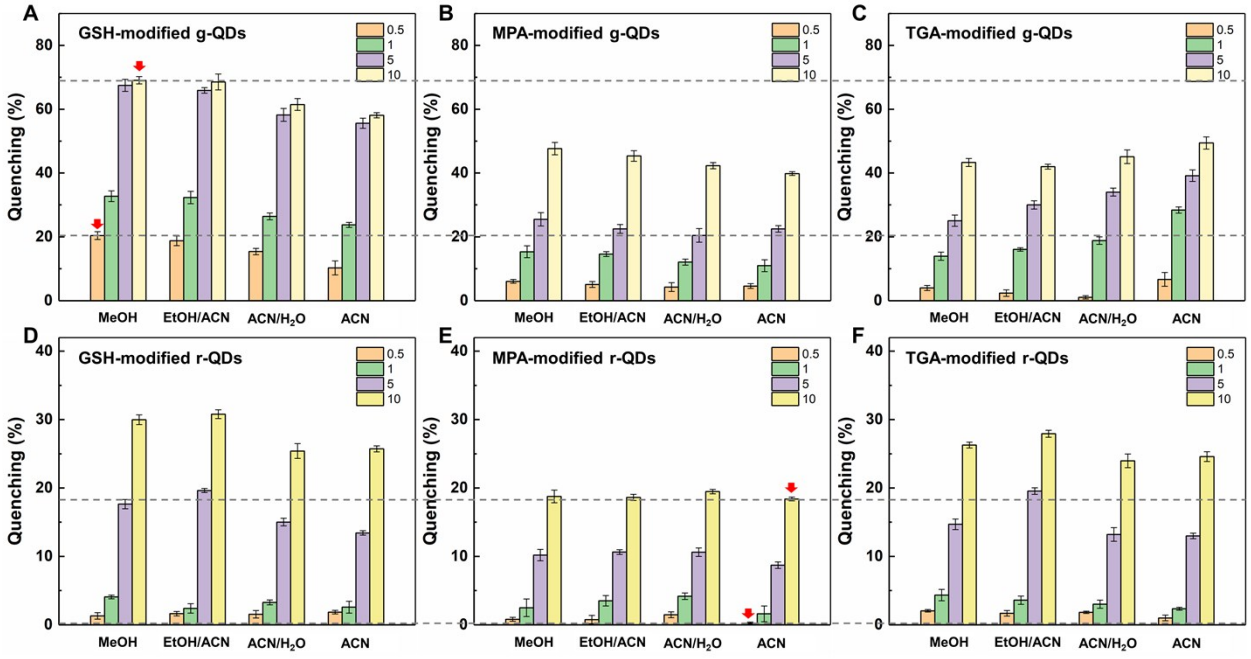


Fig. S6 Quenching degree (*i.e.*, $(I_0\text{-}I)/I_0$) of (A−C) green emission and (D−F) red emission toward 0.5−10 ppm folic acid, with different types of QDs' modifier (GSH, MPA and TGA) and eluent (MeOH, EtOH/ACN (4:1, v/v), ACN/H_2O (4:1, v/v) and ACN), respectively.

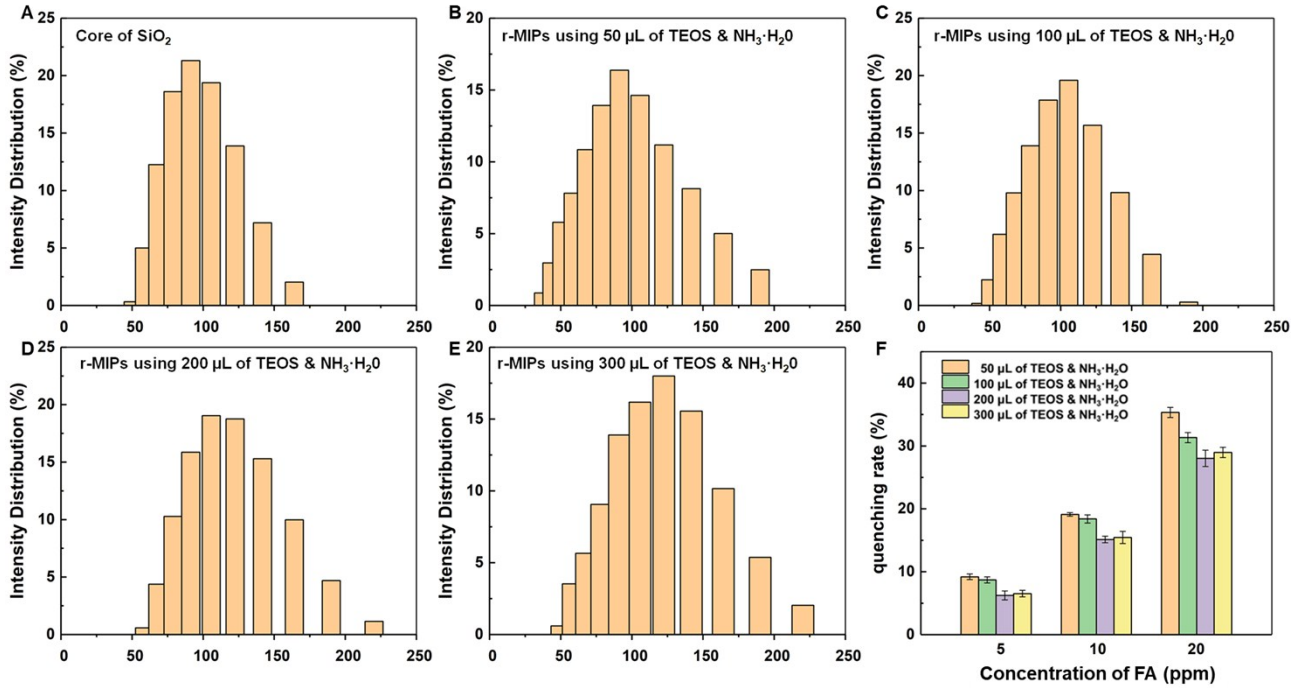


Fig. S7 Size distribution of (A) SiO_2 and r-MIPs prepared using different volumes of TEOS and $NH_3 \cdot H_2O$ of (B) 50 μL, (C) 100 μL, (D) 200 μL, and (E) 300 μL, respectively; and (F) quenching degree of r-MIPs with 5, 10 and 20 ppm folic acid, where the r-MIPs was prepared using 50, 100, 200 and 300 μL of TEOS and $NH_3 \cdot H_2O$, respectively.

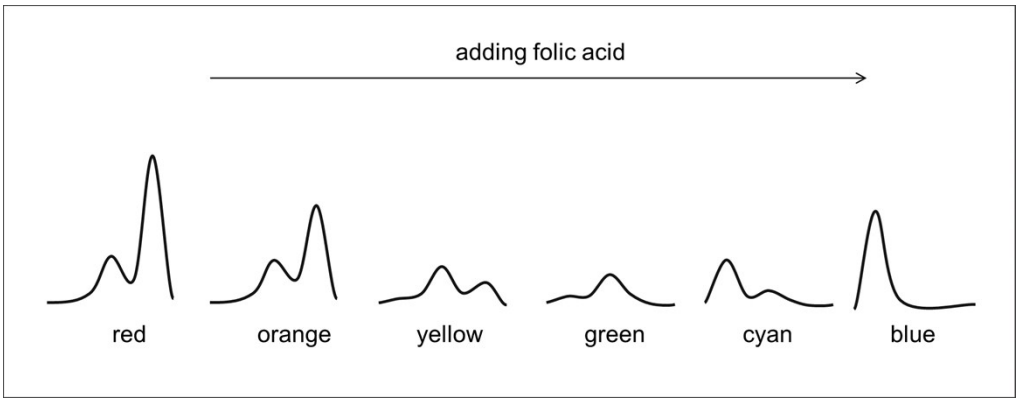


Fig. S8 Schematic diagram for the evolution of fluorescence spectra and color of triple emission MIPs sensor after the addition of folic acid, where the red emission of MIPs sensor is fast quenched but the green emission is slowly quenched.

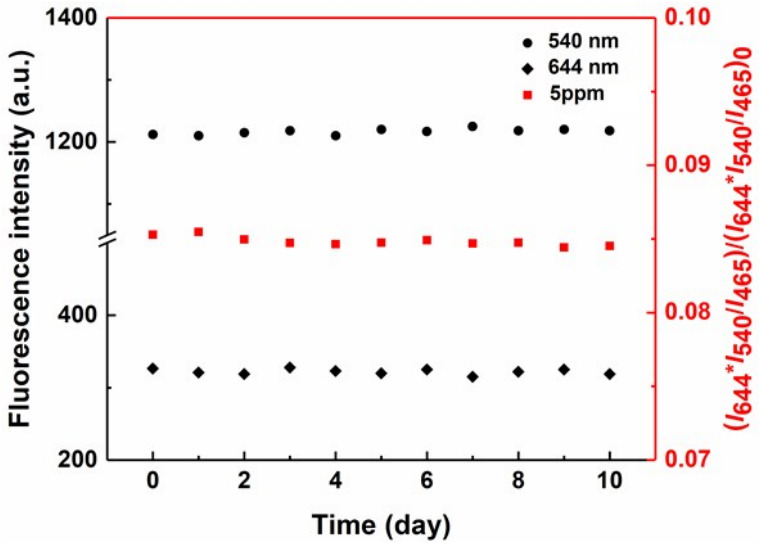


Fig. S9 The fluorescence intensities of green and red emissions before addition of folic acid (black), and ratiometric intensities of three emissions $((I_{644}*I_{540}/I_{465})/(I_{644}*I_{540}/I_{465})_0)$ after interaction with 5 ppm folic acid (red) within 10 days.