

A Novel Coumarin-Based Fluorescent Probe for the Detection of Hydrazine Both in Aqueous Solution and Vapor State

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Abstract A novel coumarin-based fluorescent probe **CF** was synthesized for the detection of hydrazine both in aqueous solution and vapor state with high sensitivity and selectivity. Upon addition of hydrazine, the solution of probe **CF** in MeCN-H₂O (3/7, v/v, buffered CH₃COOH/CH₃COONa) at pH 5.0 exhibited a remarkable change in emission color from pale green to light blue, which could be recognized with naked eyes. Applied in weak acid condition, probe **CF** could detect hydrazine selectively with large amount of unknown environments according to the competing tests. Besides, with the limit of detection 8.32 ppb (2.6×10^{-7} M), probe **CF** could well meet the request (10 ppb) of the U.S. Environmental Protection Agency (EPA).

Keywords Coumarin · Fluorescent probe · Hydrazine · Aqueous solution · Vapour state

Introduction

Hydrazine now is widely used in our daily life including medical industry, pesticide industry, space engineering and so on [1, 2]. As a highly reactive base and a strong reactant, hydrazine is playing a more and more important role in chemical

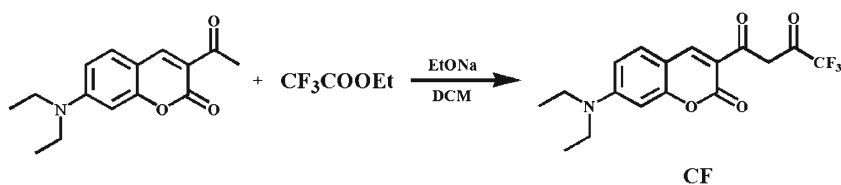
area such as the production of P-Toiuenesulfonyl hydrozide (TSH), Azobisformamide (AC). Even so, it is considered toxic by the Environment Protection Agency (EPA) with the threshold limit value (TLA) of 10 ppb [3]. In view of the character of hydrazine, scientists show a lot of interests in the detection of hydrazine. Even electrochemical techniques offer an opportunity for portable, cheap and rapid methodologies, the main drawback with the electrochemical oxidation of hydrazine is the large overpotentials at carbon electrodes [4]. Thus people found alternatives to modify the carbon surface with electrocatalysts, such as pyrogallol red [4], copper-cobalt hexacyanoferrate [5], chlorogenic acid [6], metal phthalocyanines [7], palladium nanoparticles [8]. However, the electrochemical techniques are time-consuming and troublesome in the detection of hydrazine vapors. Apart from electrochemical methods [9], flow detection [10], chemiluminescences [11] are also the traditional analytical approaches. Among these analytical approaches, spectrofluorimetry is standing out for its excellent sensitivity, high selectivity, noninvasiveness, and good compatibility for biosamples. Recent years, a lot of hydrazine detectors appeared [12–24]. All these works show that the research in the detection of hydrazine is of positive significance.

On the one hand, most of the hydrazine fluorescent probes were designed from the Schiff base based on aldehyde group's reactivity to the hydrazine [25–32]. On the other hand, a new method based on Gabriel type-based hydrazinolysis was explored to detect hydrazine recently [1, 33, 34]. Additionally, a sensitive method for the detection of hydrazine in solution was accomplished by fluorescent derivatization of hydrazine and naphthene-2, 3-dicarbaldehyde with the low limit of detection (1.6×10^{-7} M) [27]. However, the complication of getting the naphthene-2, 3-dicarbaldehyde utilized in the work limits its wide application in the detection of hydrazine. Coumarin structure is known as a widely used fluorophore because of

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Scheme 1 The synthesis of probe **CF**

its large π -conjugate system, and easy to synthesize its derivatives [13, 35–40]. Therefore, we focused on coumarin as the fundamental platform for the design of the hydrazine fluorescence probe.

The novel fluorescent probe **CF** was obtained in a simple synthetic routine and characterized by the ^1H NMR, ^{13}C NMR, IR, ESI-MS. The excellent sensitivity of **CF** toward hydrazine over other amino-group containing compounds and common ions is obvious. Upon addition of hydrazine, the solution of probe **CF** in MeCN- H_2O (3/7, v/v, buffered $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) at pH 5.0 turned on to 13-fold fluorescence enhancement, which made it easy to be distinguished.

Experimental Details

Apparatus

Melting points were determined on an XD-4 digital micro melting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer, using CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. IR spectra were collected with an IR spectrophotometer VERTEX 70 FT-IR (Bruker Optics). High-resolution mass spectrometry (HRMS) spectra were obtained on a Q-TOF6510 spectrograph (Agilent). Fluorescence measurements and UV-vis spectra were performed on a Perkin Elmer

LS-55 luminescence spectrophotometer and a U-4100 UV-vis-NIR spectrometer (Hitachi), respectively. All pH measurements involved the use of a Model PHS-3C pH meter (YouKe, Shanghai, China) at room temperature about 298 K.

Reagents

Deionized water was used throughout the experiment. All the reagents were purchased from commercial suppliers and used without further purification. The salts used in stock aqueous solutions of ions were NaNO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AgNO_3 , KNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , NaBr , NaAcO , NaCl , NaHCO_3 , NaClO , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, NaI , NaNO_3 , Na_2S , Na_2SO_3 , Na_2SO_4 . The amines used in stock aqueous solutions were $\text{NH}_3 \cdot \text{H}_2\text{O}$, CH_3NH_2 , $\text{CS}(\text{NH}_2)_2$, $\text{CO}(\text{NH}_2)_2$, $\text{HONH}_2 \cdot \text{HCl}$, $(\text{CH}_2\text{NH}_2)_2$.

Synthesis of 1-(7-Diethylamino-2-oxo-2H-chromen-3-yl)-4,4,4-trifluoro-butane-1,3-dione (Probe **CF**)

The synthetic route of the proposed probe **CF** is shown in Scheme 1. 3-Acetyl-7-diethylamino-chromen-2-one (518.6 mg, 2 mmol) was dissolved in DCM (5 mL). Then

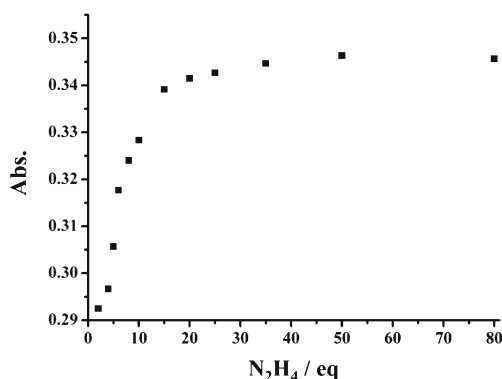


Fig. 1 Maximum absorbance (430 nm) of **CF** (10 μM) in the presence of increasing concentrations of hydrazine (0, 2.0, 4.0, 6.0, 8.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0, 80.0, 100.0 eq.) in a solution of MeCN- H_2O (3/7, v/v)

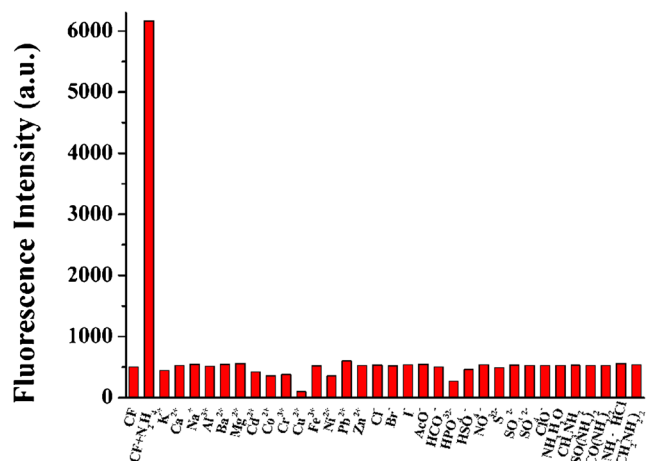


Fig. 2 The fluorescence intensity at 500 nm of the probe (1 μM) with hydrazine or various competing analytists excited at 413 nm. The competing ions were at concentration of 50 eq. of probe **CF**

trifluoro-acetic acid ethyl ester (5 mL) was added dropwise without light. After stirred at room temperature for 10 min in dark, sodium ethoxide in ethanol (5 mL, 21 %) was added dropwise with constant stirring for 4.5 h until the reaction was finished by TLC. Then 50 mL water was added and extracted with DCM (3 portions of 20 mL). The combined organic layer was washed with water, brine, and dried over anhydrous MgSO_4 . After the filtration of the MgSO_4 and the evaporation of the solvent, the crude product was recrystallized twice from ethanol to obtain a brown crystalline solid in 64.0 % yield (455 mg). mp: 205–206 °C. IR (KBr), ν : 3429, 2977, 2933, 1719, 1618, 1571, 1502, 1449, 1340, 1257, 1193, 1135, 1104, 1079, 822, 645, 571 cm^{-1} ; ^1H NMR (CDCl_3 , 300 Hz), δ (ppm): 1.27 (6H, t, $J=7.2$ Hz, CH_3), 3.49 (4H, q, $J=7.2$ Hz, CH_2Me), 6.50 (1H, d, $J=2.1$ Hz, ArH), 6.68 (1H, dd, $J=9.0$ Hz, $J=2.1$ Hz ArH), 7.43 (1H, d, $J=9.0$ Hz, ArH), 7.43 (1H, s, COCH_2CO), 8.56 (1H, s, $\text{CH}=\text{C}$); ^{13}C NMR (CDCl_3 , 75 Hz): 12.47, 45.46, 95.22, 96.84, 108.73, 110.05, 110.48, 119.16, 132.07, 147.16, 154.30, 158.32, 158.41, 178.37, 178.85, 180.08; HRMS: calcd. for $[\text{M} + \text{H}]^+$ $\text{C}_{17}\text{H}_{16}\text{F}_3\text{NO}_4$, 356.1110, found: 356.1031.

Results and Discussion

Absorption Properties

The absorption response of probe CF (10 μM) toward hydrazine was investigated (Fig. 1). The UV–vis spectral showed that with the increase of hydrazine from 2 to 100 eq., the absorbance of probe CF at around 430 nm presented an increased trend and reached the maximum with 50 eq. of N_2H_4 ,

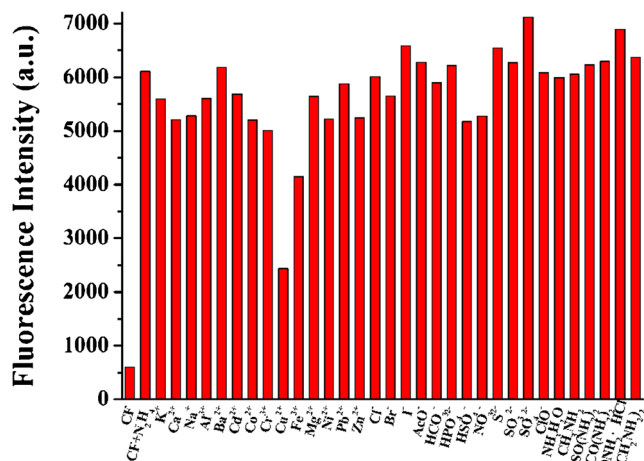


Fig. 3 Fluorescence intensity changes of CF (1 μM) and N_2H_4 (50 μM) in the presence of different analysts (50 μM) in $\text{MeCN-H}_2\text{O}$ (3/7, v/v, pH=5.0) solutions. $\lambda_{\text{ex}}=413$ nm, $\lambda_{\text{em}}=500$ nm

which implied the interaction between the probe and hydrazine.

The Selectivity of CF Over Competing Analysts

To test the selectivity of probe CF toward hydrazine, various metal ions and anions of environmental and biological abundant species were determined (Fig. 2), such as Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Na^+ , Pb^{2+} , Zn^{2+} , Br^- , AcO^- , Cl^- , HCO_3^- , ClO^- , HPO_4^{2-} , I^- , NO_3^- , S^{2-} , SO_3^{2-} , SO_4^{2-} . The results showed that CF has an excellent selectivity to hydrazine over other species even at 50 eq. of probe CF. Considered the strong nucleophilic of N within

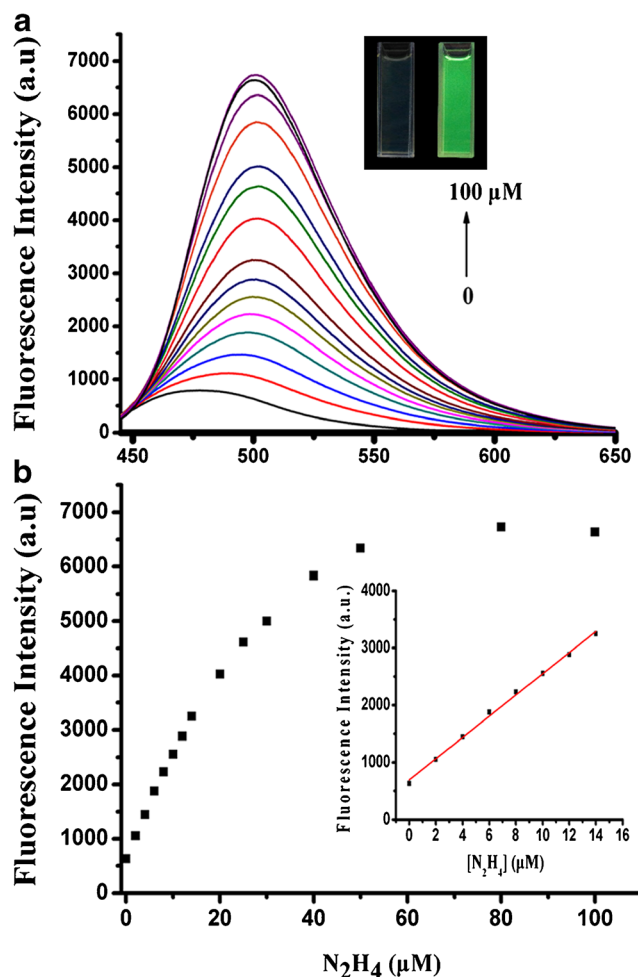
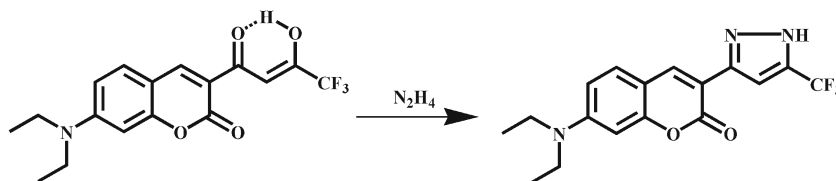


Fig. 4 a Fluorescence spectra of CF (1 μM) in the presence of increasing concentrations of hydrazine (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 4.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 50.0, 80.0, 100.0 eq.) at pH 5.0, $\text{MeCN-H}_2\text{O}$ (3/7, v/v) with excitation at 413 nm. *Inset*: the color change observed by the naked eyes of probe CF with the addition of hydrazine b Change of fluorescent intensity (500 nm) of the solution when excited at 413 nm. *Inset*: The linearly relationship between the concentration of the fluorescence intensity and hydrazine

Scheme 2 Proposed mechanism of the detection of hydrazine



N_2H_4 , we also examined whether other amines with nucleophilic N atoms such as ammonia, methylamine, ethanediamine, hydroxylamine, carbamide, thiocarbamide interfered the detection of hydrazine under the same condition. These species did not exert interferences, which lead us to make sure that **CF** could be used to detect hydrazine selectively even in complex environment.

Tolerance Over Other Species

In order to explore the further application, competition experiments were also carried out (Fig. 3). Upon the addition of hydrazine to the solution of **CF** (1 μM) containing of various ions (50 μM) and other amines (50 μM), the fluorescence intensity of the solution was still obviously higher than the referenced solution except Cu^{2+} , which may be due to its own electronic characteristics [41]. On this basis, **CF** could successfully undergo a hydrazine-induced cyclization to give a fluorescence enhancement product even in the presence of other potentially competitive ions and amines.

N_2H_4 -Titration and Limit of Detection

Consistently, the concentration-dependent changes of the fluorescence spectra of **CF** (1 μM) with hydrazine were explored under the same condition (Fig. 4a). The results showed that with increasing concentrations of hydrazine, probe **CF**

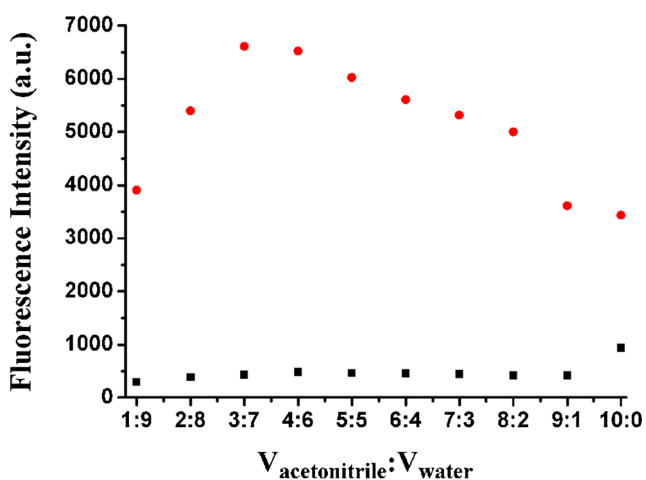


Fig. 5 Fluorescence intensity of probe **CF** in the presence of N_2H_4 at different ratios of MeCN : H_2O (pH 5.0) with the excitation at 413 nm

presented a large fluorescence turn-on response toward hydrazine accompanied by a 22 nm red shift and the fluorescence intensity fitted linearly with the concentration of hydrazine from 0 to 14 eq ($R^2=0.997$) (Fig. 4b). The detection limit based on IUPAC was 2.6×10^{-7} M (8.32 ppb). And the fluorescence quantum yield of **CF** is 0.265 in the condition of fluorescence intensity being 6730.5 a.u..

The Proposed Reaction Mechanism

The mechanism of the change should be due to the conjugation system in probe **CF** was changed by reacting with hydrazine followed by a cyclized product, which may be contributed to the red shift of the fluorescence emission (Scheme 2). A possible interaction between probe **CF** and N_2H_4 is also suitable for the similar phenomenon in the fluorescence titration plot of other N_2H_4 probes [42].

The Effect of the Volume Fraction of MeCN in Water

As we all know, MeCN is toxic to environment and can do harm to our health like N_2H_4 dose as an organic reagent. Therefore, to limit the use of MeCN in our testing system is notable. The fluorescence intensity of the solution with hydrazine under the condition of 3:7 (v/v, MeCN : H_2O) was about 13 times more than it without hydrazine, whose sharp contrast in

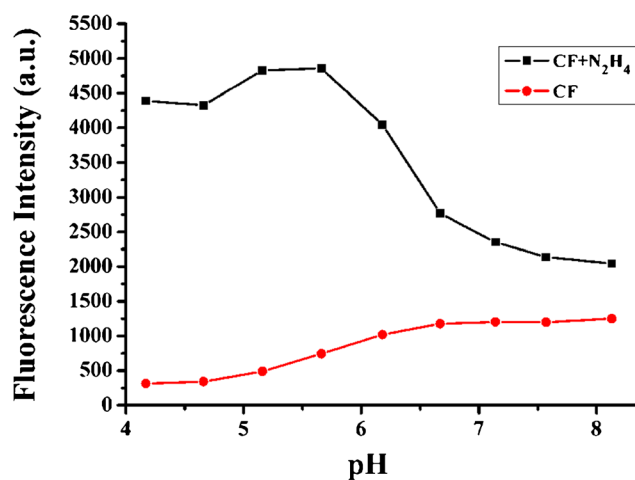


Fig. 6 Fluorescence intensity changes of **CF** (1 μM) and N_2H_4 (100 μM) with respect to different pH levels, in MeCN- H_2O (3/7, v/v) solutions. $\lambda_{\text{ex}}=413$ nm, $\lambda_{\text{em}}=500$ nm

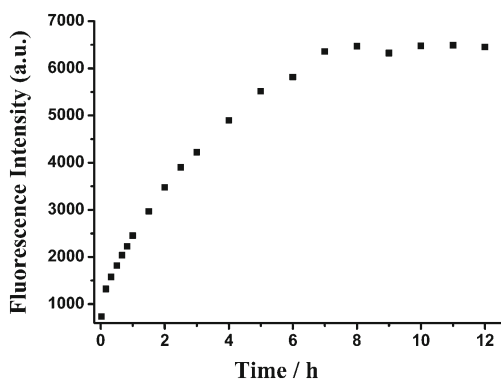


Fig. 7 Time-dependent fluorescent intensity of probe **CF** (1 μ M) in the presence of N_2H_4 (50 eq.) in MeCN- H_2O (3/7, v/v, pH=5.0) solutions. λ_{ex} =413 nm, λ_{em} =500 nm

fluorescence spectra showed that **CF** can perform a best response to recognize N_2H_4 obviously (Fig. 5).

pH Dependent Studies

Considering the effect of H^+ both for **CF** and **CF**+ N_2H_4 , pH from 4.0 to 8.0 were tested (Fig. 6). The result showed that the largest increased times of fluorescence intensity was appeared at pH 5 after the addition of N_2H_4 , which demonstrated that **CF** could achieve the detection of hydrazine under such weak acid condition.

Time-Dependent Fluorescence Changes of **CF** Toward Hydrazine

Then time course of the fluorescence intensity of probe **CF** (1 μ M) in the presence of hydrazine (50 μ M), (MeCN- H_2O , 3/7, v/v, pH 5.0) at emission being 500 nm was recorded (Fig. 7). The emission enhancement at different time intervals was observed as time going by. The plots showed that the fluorescence intensity gradually peaked at about 9 h. Even

though it took a long time, the fluorescence intensity was increased about 13-fold after reacting for 9 h, which was so significant that could be recognized easily.

Application of Probe **CF**

In view of the practical application of probe **CF**, we further tested whether **CF** could distinguish hydrazine vapor. TLC plates were immersed in a MeCN solution of **CF** (0.1 mM) for 30 s. When dried, the probe-loaded TLC plates were covered at the top of a screw bottle containing an analyte solution for 5 min at room temperature before observation. As shown in Fig. 8, the distinctive changes of fluorescence color (from light green to light blue) were obvious under the circumstances of different concentrations of hydrazine vapor. Otherwise, there was not distinguished change in fluorescence when the TLC plates were exposed to the air for a period of time, from which we could conclude that the TLC plates coated with **CF** were insusceptible from the gas like H_2O , CO_2 , O_2 and other analytes. These results confirmed that **CF** can not only test hydrazine in solution but also response to it upon its vapor state.

Conclusion

A new fluorescent probe **CF** based on coumarin fluorophore has been designed and synthesized for detecting hydrazine. The probe undergoes a mechanism of five-membered heterocyclic compound, which embodies its high sensitivity and selectivity toward hydrazine at weak acid condition with a low detection limit. With low toxic solvent, **CF** revealed an environmentally friendly characteristic. The ability of anti-interference makes it possible to test hydrazine both in solution and vapor state accurately under an unknown circumstance.

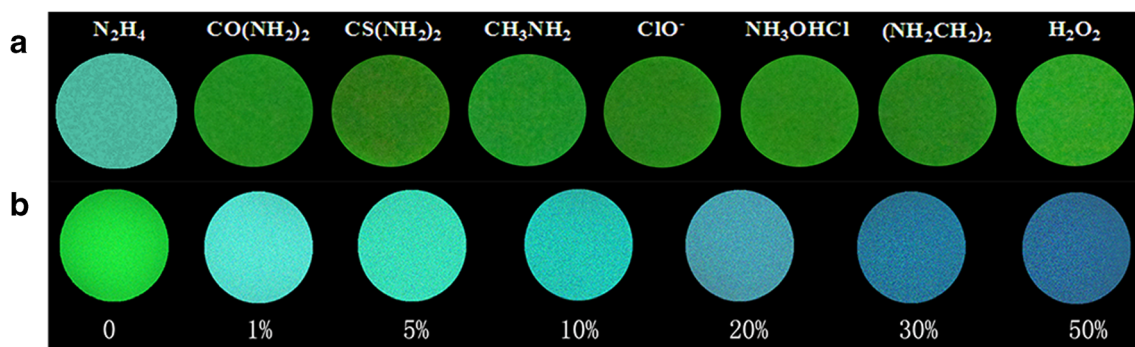


Fig. 8 **a** Fluorescence color changes of **CF** (0.1 mM)-coated TLC plates after exposure to different analytes (10 mM). **b** Fluorescent color changes of **CF** (0.1 mM)-coated TLC plates after exposure to different

concentrations of hydrazine aqueous solution. The fluorescent color changes were observed using a hand-held UV lamp with an excitation at 365 nm

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