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A coumarin based chemodosimetric probe for ratiometric detection of hydrazine

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ABSTRACT

A coumarin-based sensor containing trifluoroacetyl acetonate moiety was designed, synthesized, and applied for hydrazine detection. Hydrazinolysis of the chemodosimeter results in a prominent chromogenic and fluorescence ratiometric response toward hydrazine within 3 min. The probe is highly selective toward hydrazine over other important amines and other biologically and environmentally abundant analytes. The limit of detection (LOD) of the probe is in 10^{-6} M range. The sensing mechanism was supported by NMR and HRMS analysis. The experimentally observed change in structure and electronic properties of the sensor after reaction with hydrazine was modeled by Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TDDFT) computational calculations, respectively.

In recent era, the development of chemosensors as well as chemodosimeters for the recognition of environmentally important and hazardous analytes has been receiving considerable attention.[1] Hydrazine pollution is a global problem and creates a significant damage to human health. Hydrazine is extensively used as a high energetic fuel in missile propulsion systems.[2,3] It is a highly explosive base and a robust reducing mediator and is used as a key reactant in the preparation of pharmaceuticals, photography chemicals, pesticides, dyes, and emulsifiers.[4] Nevertheless, hydrazine has considerable effects that can potentially lead to serious environmental pollution during its production, use, conveyance, and clearance. Hydrazine is routinely determined by electrochemical analysis[5] and chromatography,[6] including gas chromatography,[7] HPLC,[8] and capillary electrophoresis.[9] Due to its extensive applications and poisonous effects, it is highly desirable to develop consistent and sensitive analytical methods for the selective detection of hydrazine. However, there are only a few reports regarding hydrazine-assisted fluorescent probes.[10]

In continuation of our research work in the development of fluorescence sensors[11] for important analytes, herein, we disclose the design and synthesis of a fluorescence sensor based on coumarin-trifluoroacetyl acetonate moiety (CTF; C = coumarin, TF = trifluoroacetyl acetonate) which can selectively detect hydrazine ratiometrically in acetonitrile media. Hydrazine plays here the key role to affect the ICT distribution of CTF through the formation of a five-membered ring in its side chain, therefore a subsequent ICT-induced ratiometric response was observed both in absorption and fluorescence changes toward hydrazine. As depicted in Scheme 1, compound **1** [3-acetyl-7-(diethylamino)coumarin] was synthesized by following a similar procedure reported earlier.[12] Compound **1** was converted to the target sensor CTF [1-(7-(diethylamino)-2-oxo-2*H*-chromen-3-yl)-4,4,4-trifluorobutane-1,3-dione] by treatment with ethyl trifluoroacetate through Claisen condensation in 64% yield. The structure of CTF was confirmed by ^{1}H NMR, ^{13}C NMR, (^{1}H–^{13}C) HMBC NMR, and HRMS spectroscopy (Supplementary data Figs. S7–S11).

In this Letter, a new signaling probe (CTF) was devised for hydrazine, using selective hydrazinolysis at the carbonyl group of trifluoroacetyl acetonate moiety followed by cyclization to give ultimately a new fluorescent species (CTF–N_2H_4). We observed here that the sensor CTF can react with hydrazine to generate CTF–N_2H_4 (7-(diethylamino)-3-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one) with a ratiometric fluorescence response as shown in Scheme 2.

The absorption and emission properties of the probe were investigated by addition of very small amount of hydrazine; it causes the signal to change rapidly. CH_3CN was selected as an analysis solvent to explore the optical response of CTF toward hydrazine at room temperature. UV–vis spectral studies of CTF (10 μM, CH_3CN, 25 °C) exhibited the maxima around at 485 nm. Upon addition of hydrazine (2×10^{-4} M in CH_3CN), the absorption at 485 nm

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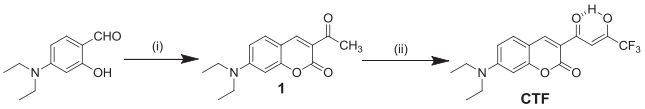
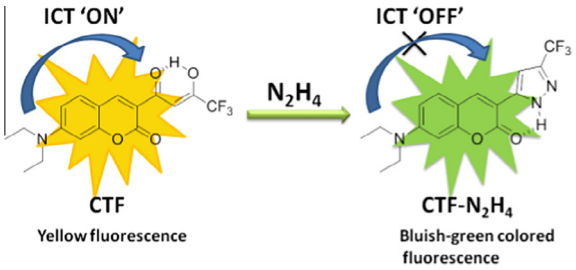


Scheme 1. Synthetic scheme of the probe (CTF). Reagents and conditions: (i) ethyl acetoacetate, EtOH, piperidine, reflux, 6 h; (ii) ethyl trifluoroacetate, NaOMe, DCM, reflux, 1 h.



Scheme 2. Probable sensing mechanism of CTF with N_2H_4.

eventually decreased, whereas two new absorption peaks gradually appeared at 445 and 395 nm with two isosbestic points arising at 273 and 335 nm. Such a blue shift (most prominent one) of 90 nm causes a change in the absorption behavior showing the change in the color of the solution from orange yellow to light green, which allows a colorimetric detection of hydrazine to the naked eye (Fig. 1). Now, the experimental data showed that in the presence of 1.5 equiv of hydrazine ratiometric value increases (A_{395}/A_{485}, from 0.7315 to 1.9094), which was observed with respect to CTF itself and ratio of two absorbance intensities (A_{395}/A_{485}) maintained a good linear relationship with the concentration of hydrazine ($R^2 = 0.994$).

Fluorogenic studies of CTF were investigated in CH_3CN solution. Here also the spectral property of CTF was found to perturb only by hydrazine. Upon excitation at 450 nm CTF (10 μM, CH_3CN, 25 °C) shows a maxima at 545 nm ($\varphi = 0.01$) in the absence of any analyte. Upon incremental addition of hydrazine the peak at 545 nm decreases regularly and a new peak at 500 nm increases ($\varphi = 0.11$) rapidly and consequently it leads to a blue-shift from 545 to 500 nm (Fig. 2). The experimental data showed that the emission intensity ratio (I_{500}/I_{545}) of CTF after addition of hydrazine fits linearly with hydrazine concentration, having a good R^2 value of 0.995. The detection limit was found to be 3.38×10^{-6} M. The

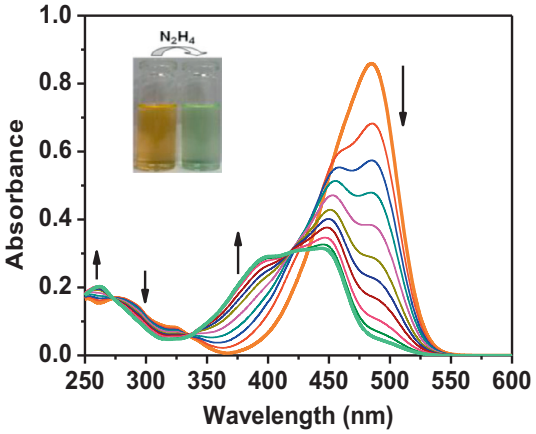


Figure 1. (a) Change of UV–vis spectra of CTF (10 μM) upon gradual addition of hydrazine (0–2 equiv). Inset: Visible color change observed in CTF in absence and presence of 2 equiv of hydrazine.

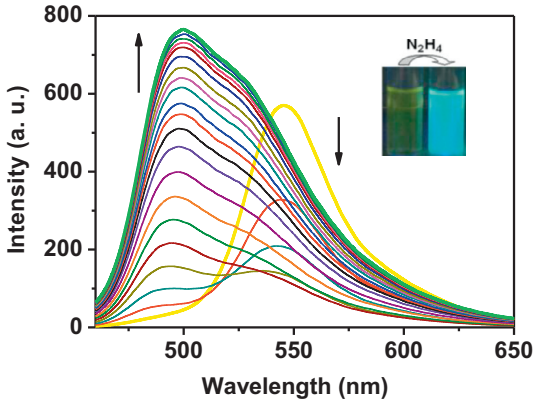


Figure 2. (a) Change of fluorescence spectra of CTF (10 μM) upon gradual addition of hydrazine (0–2 equiv). Inset: Visible emission observed from CTF in absence and presence of 5 equiv of hydrazine after irradiation under UV light.

mechanism of this type of change may be explained by the addition of hydrazine. After reaction with hydrazine the conjugation is being hampered, that is, ICT (intramolecular charge-transfer) turning off, which is accompanied by the blue-shift in fluorescence. In contrast, only an insignificant change was observed upon the addition of different amines, for example, ethylenediamine, dimethylamine, triethylamine, NH_2OH, piperazine, phenylhydrazine, etc. Noteworthy is that it gains much importance that even after addition of about 10 fold excess of these test amines, there was no perturbation of the hydrazine-induced fluorescence response. The effect of environmentally as well as biologically important ions such as Na^+, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Hg^{2+}, Cd^{2+} (as their chloride salts), S^{2-}, HSO_3^-, SO_4^{2-}, NO_3^- and N_3^- (as their sodium salts) was also examined and there was no significant change observed both in UV–vis and fluorescence titration experiments.

Now the reaction of CTF with hydrazine might proceed through the formation of a five-membered cyclized product (CTF–N_2H_4) (Scheme 2, Figs. 3 and 4). Here the trifluoroacetyl acetone moiety

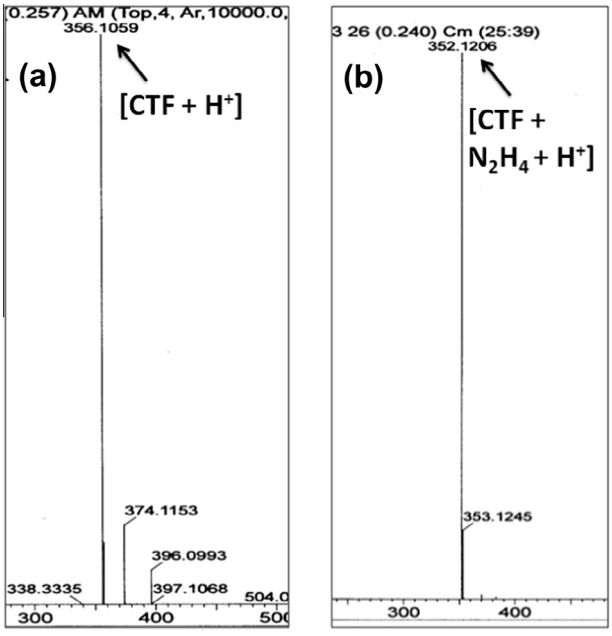


Figure 3. Partial HRMS spectra (a) of CTF and (b) [CTF–N_2H_4] the product resulting from reaction of CTF with hydrazine.