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A highly selective long-wavelength fluorescent probe for hydrazine and its application in living cell imaging

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Abstract

A highly selective long-wavelength turn-on fluorescent probe has been developed for the detection of N_2H_4.The probe was prepared by conjugation the tricyanofuran-based D-π-A system with a recognizing moiety of acetyl group. In the presence of N_2H_4, the probe can be effectively hydrazinolysized and produce a turn-on fluorescent emission at 610 nm as well as a large red-shift in the absorption spectrum corresponding to a color change from yellow to blue. The sensing mechanism was confirmed by HPLC, MS, UV-vis, emission spectroscopic and theoretical calculation studies. The probe displayed high selectivity and sensitivity for N_2H_4 with a LOD (limit of detection) of 0.16 μM. Moreover, the probe was successfully utilized for the detection of hydrazine in living cells.

Keywords: Fluorescent probe, Red emission, Hydrazine detection, Cell imaging

1. Introduction

Hydrazine is a small, difunctional and highly reactive regent with good reducing capabilities and can participate in diverse reactions in numerous applications [1]. Hydrazine has been wildly used as fuel for rockets and fuel cells as well as employed as starting material for many derivatives such as antioxidants, polymers, foaming agents for plastics, pesticides and pharmaceutical products [2-4]. But on the other hand, hydrazine is highly neurotoxic, hepatotoxic, mutagenic, carcinogenic and adverse health effects. It can be intaken by human beings through skin absorption or respiration, and may cause many symptoms such as headache, seizures, convulsions, irritation, liver and kidney damages etc [5-7]. As consequence, hydrazine has been considered to be hazardous pollutant by the U.S. Environmental Protection Agency (EPA) and its threshold limit value (TLV) was suggested to be 10 ppb [8]. It is therefore obvious that the development of simple, sensitive, accurate and rapid analytical methodologies for the determination of hydrazine are highly required for human health and safety.

There have been many methods reported to detect and quantify hydrazine, such as derivatization approach coupled with chromatography techniques ranging from GC–MS (gas chromatography-mass spectrometry) [9-11], LC–MS (liquid chromatography-mass spectrometry) [12, 13], CE (capillary electrophoresis) [14], electroanalytical techniques based on modified electrodes with deposited films of various nanocomposites [1, 12, 15-21]. But these methods typically require special equipment and sophisticated sample preparation, as well as consuming time and unamenable real-time and on-site detection. Recently, a great deal of attention has been given to develop fluorescent probes for detecting hydrazine due to their high sensitivity and selectivity, economy, simplicity for implementation, spatiotemporal

resolution, noninvasiveness and good compatibility for biosamples. These reported fluorescent probes have been designed mainly based on the reaction of hydrazine with various recognizing moieties, including aldehyde [22-24], γ-bromobutyrate [25-28], acetyl [29-32], levulinate [33, 34], and phthalimide [35-38], et al. Most of these developed fluorescent probes show emission and absorption within ultraviolet or short-wavelength range and are not suitable for bioassays. Fluorescent probes with both excitations and emissions in long-wavelength region are more favorable for practical measurements, due to the weak antofluorescence interference from the complex matrix, minimum photodamage, and good tissue penetration [39-41].

2-Dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF), as a strong electron acceptor, was initially used for preparation nonlinear optical materials [42-45], and recently was successfully exploited for construction red-emission fluorophores for detection of K^+ [46], H^+ [47], biothiols [48], the activities of bioenzymes [49, 50], as well as for bioimaging [51, 52]. Herein, based on the TCF fluorophore, a new red-emission fluorescent probe (**1**) for N_2H_4 detection was developed. A phenolic hydroxyl group donor was first connected to a TCF acceptor via a conjugated π-bonded network to afford 1-(3-cyano-2-dicyanomethylen-5,5-dimethyl-2,5-dihydrofuran-4-yl)-2-(4-hydroxylphenyl) ethane (**2**) which exhibited excellent red emission features (em: 610 nm, ex:580 nm). Probe **1** was obtained by caging the donor group (phenolic hydroxyl) of **2** with acetyl group, and probe **1** displayed nonemmision in red light region due to the blockage of the ICT (intramolecular charge transfer) progress by the introduced electron-withdrawing moiety (acetyl group). In the presence of N_2H_4, the acetyl group of probe **1** can be selectively cleaved resulting the restoration of compound **2**, and large bathochromic shift in the absorption spectra as well as the significant enhancement in fluorescent

emission. Thus, a highly sensitive and selective trun-on fluorescent assay was successfully developed for the detection of hydrazine. Moreover, Cell imaging studies implicated that the probe can be exploited to detect hydrazine in biological systems.

2. Experimental

2.1. Materials and instrumentations

All reagents were obtained from commercial suppliers and used as received without further purification unless otherwise noted. All solvents for analytical tests were HPLC reagent grade. Deionized water obtained by using a Milli-Q Plus system (Millipore Corp., Bedford, MA, USA) was used throughout the experiments. ^{1}H NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer. Chemical shifts were internally referenced to tetramethylsilane. Mass spectrometry was performed on a Waters ® Xevo G2- S QTof™ mass spectrometer (Waters, Milford, MA, USA). The fluorescence spectra were carried out on a with a Varian Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Santa Clara, USA). The absorbance spectra were recorded with a Cary 60 UV–Vis spectrophotometerAgilent (Agilent Technologies, Santa Clara, USA).

2.2. UV−Vis absorption and fluorescence spectroscopy analysis

Stock solution of probe **1** was prepared in DMSO. Hydrazine and other relevant analytes were prepared in water. Stock solution of **1** was diluted to the desired concentration with buffered H_2O/DMSO (9/1, v/v; pH = 8.0; HEPES, 10 mM). All measurements were performed in a mixed solution of HEPES buffer:DMSO = 9:1 (v/v, pH 8.0, 10 mM) at room temperature. Samples for absorption and emission measurements were contained in quartz cuvettes (3 mL volume). For fluorescence tests, the excitation and emission slit width were both set at 5 nm.

2.3. HPLC analysis

HPLC analysis was performed was performed on a Waters Acquity UPLC H-Class system (Milford, MA, USA) equipped with a quaternary solvent delivery system, a column oven, an auto sampler, and a photodiode array detector. The analytes were separated in gradient mode with a Waters ACQUITY BEH 2.1 × 50 mm C18 1.7 μm column. The column oven was kept at 40 ^{o}C. Flow rate was 0.5 mL/min. Eluent components were water contained 0.1% formic acid (A) and acetonitrile contained 0.1% formic acid (B). The mobile phase gradient was as follows: A/B = 50/50 (0 min) - A/B = 0/100 (1.5 min).

2.4. Fluorescence imaging

The cultured Hela cells were incubated with probe **1** (10 μM), probe **1** (10 μM) and consequently with N_2H_4 (100 μM) in DMEM (Dulbecco's Modified Eagle Medium) at 37 ^{o}C, respectively. The incubation time was set at 30 min. After incubation for the corresponding time, the cells were washed with PBS three times to remove free compound and ions before analysis. Then the cells were imaged on confocal microscope (Olympus, FV1000, Japan).

2.5. Cell viability assay

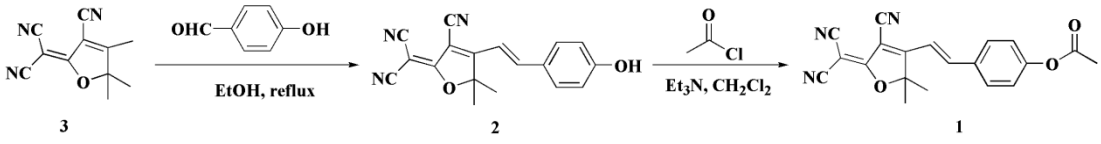
The toxicity of probe **1** towards living cells was determined by MTT (3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2-H-tetrazolium bromide) assays. Two kinds of cell liens (HeLa and A549 cells) were evaluated. The cells were seeded in 96-well plates at a density of 5×10^3 cells per well and cultured for 24 h at 37 ^{o}C with 5% CO_2 in humidified environment. Then a series of different concentrations of probes (0, 5, 10, and 20 μM) were added to the separated wells, and the cells were incubated for an additional 24 h. MTT solution was then added into each well and then residual MTT

solution was removed after 4 h. The MTT-formazan crystals were dissolved in 200 μL DMSO. The absorbance of each well was measured by a microplate reader (Bio-TekELx800) at the wavelength of 490 nm. The cell viability was assessed using the following Equation: Cell viability (%) = $A_T/A_0 \times 100\%$, where A_T is the absorbance of treated cells and A_0 is the control absorbance. Data of cell viability are given as mean ± standard deviation (S.D.) (three replicate measurements).

*2.6. Synthesis of probe **1***

Compound 1-(3-cyano-2-dicyanomethylen-5,5-dimethyl-2,5-dihydrofuran-4-yl)-2-(4-hydroxylphenyl) ethane (**2**) were prepared by adapting published procedures [53].

To a mixture of **2** (303 mg, 1.0 mmol) in dichloromethane (10 mL) was added acetyl chloride (0.142 mL, 2.0 mmol) and triethylamine (0.304 mL, 2.2 mmol). The resulting solution was stirred overnight. After removal of the solvent, the obtained residue was purified over silica gel using using dichloromethane/methanol (10/1, v/v) as the eluent to afford the desired probe as a yellow solid (289 mg, 84%). ^{1}H NMR (400 Hz, $CDCl_3$): δ 7.61 (d, J = 7.9 Hz, 2H), 7.55 (s, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 16.4 Hz, 1H), 2.27 (s, 3H), 1.66 (d, J = 58.5 Hz, 6H) (see Fig. S1). HRMS: m/z, calcd for $[M+H]^+$ 346.1192; found 346.1167 (see Fig. S2).



Scheme 1 Synthesis of probe **1**.

3. Results and Discussion

*3.1. Synthesis of Probe **1***

Probe **1** could be readily synthesized with TCF as the starting materials through two-step reactions as illustrated in Scheme 1. First, The electron acceptor TCF was condensed with a moiety *p*-hydroxybenzaldehyde in ethanol to afford compound **2**. Then, the phenolic hydroxyl of **2** was grafted with acetyl group to produce the final product **1** which was characterized by ^{1}H NMR and HRMS. Due to the attenuated electron donating ability of the formed acetyl ester group, probe **1** completely switched off the fluorescence of compound **2** in red spectral region.

*3.2. Spectral response of probe **1** to hydrazine*

Acetyl was chosen as the recognition moiety for sensing hydrazine. Due to the strong electron withdrawing, substitution by acetyl can greatly change the electron distribution of a probe and its spectral properties. When attacked by hydrazine, the acetyl group can be released and lead to the restoration of spectral features for the original fluorophore. We primarily assessed the spectral properties of probe **1** in a mixture of aqueous HEPES buffer (10 mM, pH 8.0) and DMSO (9:1, v/v). The solution of probe **1** showed a major absorption maximum absorption at about 400 nm and none emission (curve a, Fig. 1 A). Upon the addition of (20 equiv) N_2H_4 to the solution, the absorbance at 400 nm evidently decreased with the appearance of a new absorption band centered at 580 nm (curve b, Fig. 1 A). This significant bathochromic shift (180 nm) in absorption spectra can be ascribed to the enhanced ICT process of the fluorophore, which was confirmed by the spectral features of the fluorophore in different solvents (see Fig. S3). A distinct color change of the probe solution from yellow to purple upon the addition of N_2H_4 can be clearly observed, signifying the capability of probe **1** for the colorimetric detection of hydrazine by naked eyes (Fig. 1 A, inset). Consistently, co-incubation of probe **1** with hydrazine led to the significant enhancement of a fluorescence emission band at 610 nm (upon excitation at 580 nm)

(Fig. 1B).

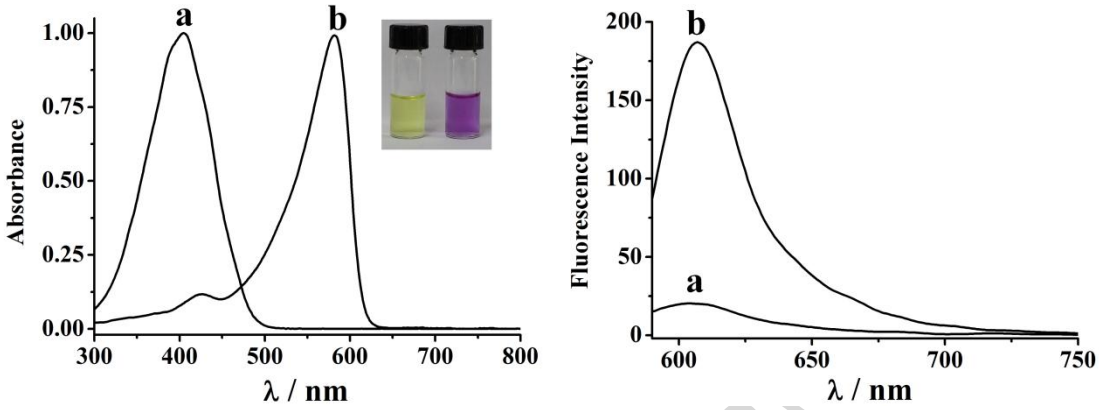


Fig. 1 (A) Normalized absorption and (B) fluorescence emission spectra of probe **1** (10 μM) before (a) and after (b) reaction with N_2H_4 (200 μM) for 1 h in HEPES buffer (10 mM, pH 8.0, 10% DMSO), λ_{ex} = 580 nm. The inset show their corresponding photographic images.

*3.2. Fluorescence spectra of probe **1** titrated with hydrazine*

Quantitative off-on responses of probe **1** to hydrazine were investigeted by fluorometric titrations. The emission spectra of probe **1** (5 μM) in the presence of different concentration of hydrazine from 1 to 100 μM were recorded. As shown in Fig. 2A, the fluorescence intensity at 610 nm gradually enhanced with increasing hydrazine concentration, and a good linear relationship between the fluorescence intensity and hydrazine concentrations in the range of 0 to 50 μM. The regression equation was $I = 2.308\times[N_2H_4]/\mu M + 29.28$ ($R^2 = 0.997$). The LOD (limit of detection) of the assay for hydrazine was calculated to be 0.16 μM (S / N = 3) which is lower than the threshold limit value (0.3 μM) set by EPA [8]. The performances of probe **1** for hydrazine detection were also compared with other recently reported fluorescent probes based on the recognition moiety of acetyl, as shown in Table S1,

the proposed probe exhibited comparable or superior analytical performances compared to others [54-59].

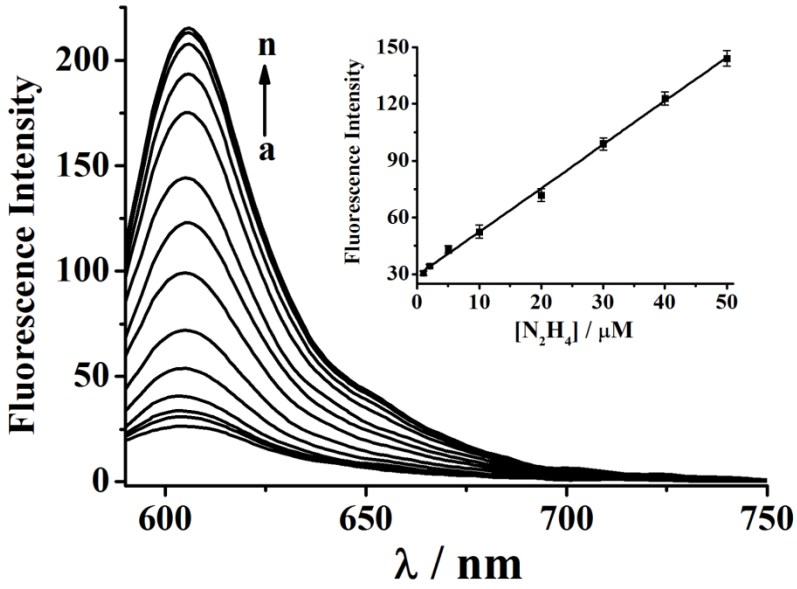


Fig. 2 (A) Fluorescence spectra of **1** (5 μM) in the presence of various concentrations of N_2H_4, from (a) to (n), 0, 1.0, 2.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0 90.0 and 100.0 μM. (B) The linear fitting curve between the fluorescence intensity (*I*) and the concentration of N_2H_4. λ_{ex} = 580 nm.

Reaction rate is a key factor for the optical response of the probe for hydrazine. Therefore, we investigated the response dynamics of probe **1** to hydrazine. Probe **1** showed a significant increase in fluorescence emission with reaction time, and a plateau of intensity changes could be achieved within 60 min upon addition of 20 equiv of hydrazine (see Fig. S4). Therefore, 60 min was selected as the optimum reaction time.

*3.3. Selectivity of probe **1** toward hydrazine*

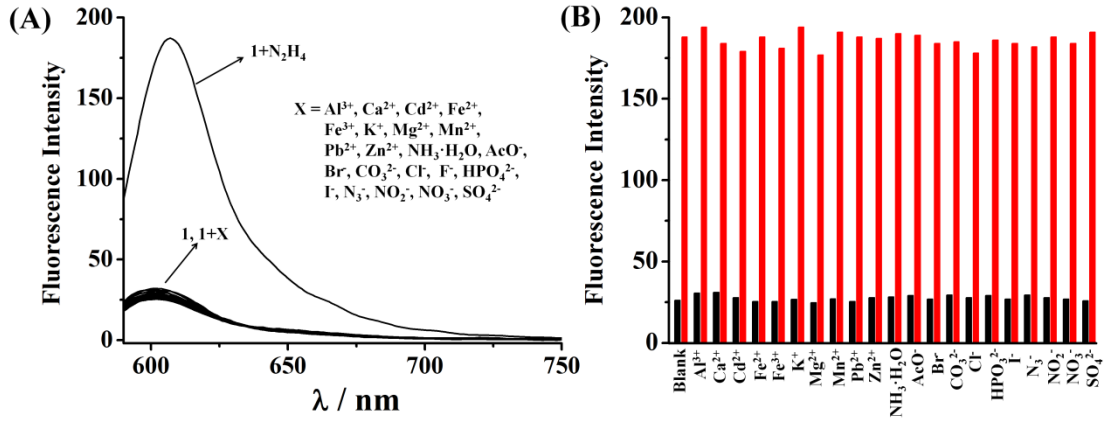
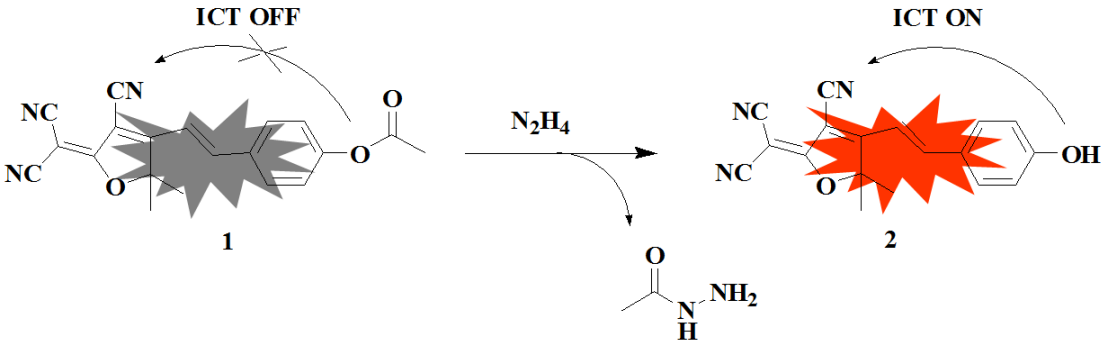


Fig. 3 (A) Fluorescence changes of **1** (5 μM) to hydrazine (100 μM) and various metal ions or anions (100 μM). (B) Fluorescence responses of **1** (5 μM) in the presence of different metal ions or anions (100 μ M) (low bars), followed by addition of hydrazine (100 μM) (high bars). λ_{ex} = 580 nm.

An important feature of a chemosensor is the high selectivity towards the analyte over other interferences. To evaluate the selectivity of the proposed probe, we examined the fluorescence response of 1 to various interferences including Al^{3+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, $NH_3{\cdot}H_2O$, AcO^{-}, Br^{-}, CO_3^{2-}, Cl^{-}, F^{-}, HPO_4^{2-}, I^{-}, N_3^{-}, NO_2^{-}, NO_3^{-}, SO_4^{2-}. As shown in Fig. 3A, other interferences did not lead to any significant fluorescence enhancement of **1** at 610 nm, while a evident emission band was observed upon addition of N_2H_4. Moreover, competition experiments were conducted to study the influence of other analytes on N_2H_4 detection by using probe **1**. Similar fluorescence responses of probe **1** to hydrazine were observed regardless of the presence or absence of various other interferences (Fig. 3B). These results demonstrated that probe **1** could offer high specifically for hydrazine detection.

3.4. Sensing mechanism



Scheme 2 Proposed sensing mechanism of probe **1** toward N_2H_4.

The reaction of probe **1** with hydrazine is expected to produce compound **2**, due to the selective deprotection of the acetyl group of probe **1**. Based our experimental results and reported literatures, the reaction mechanism of probe **1** with hydrazine involved the nucleophilic addition of hydrazine at the carbonyl position of acetyl and then lead to the cleavage of the ester group and the restoration of compound **2** (scheme 2). This transformation was confirmed by HPLC, MS, UV-vis and emission spectroscopic studies. The maximum absorbance and emission at 580 nm and 610 nm of the hydrazine-treated probe solution were consistent with that of compound **2**. Furthermore, probe **1**, compound **2**, and the reaction product of probe **1** with hydrazine were identified by HPLC analysis (Fig. 4). Probe **1** alone showed a single peak with Rt (Retention time) of 0.99 min (Fig. 4A). After mixing probe **1** with 5 equiv N_2H_4, a new peak with a Rt of 0.63 min appeared (Fig. 4B). When probe **1** was mixed with 20 equiv N_2H_4, the peak at 0.99 min completely disappeared leaving only a peak at 0.63 min which was identical to that of compound **2** (Fig. 4D). These results suggested that the probe **1** was converted to **2** by hydrazinolysis. For additional evidence to support our proposed mechanism, mass spectroscopy was also used to analyze the reaction product of probe **1** with hydrazine. After incubation solution

displayed a new peak at m/z 304.1042 $[M+H]^+$ which was corresponding to the protonated compound **2** ([M+H]+, m/z 304.1026) (see Fig. S5).

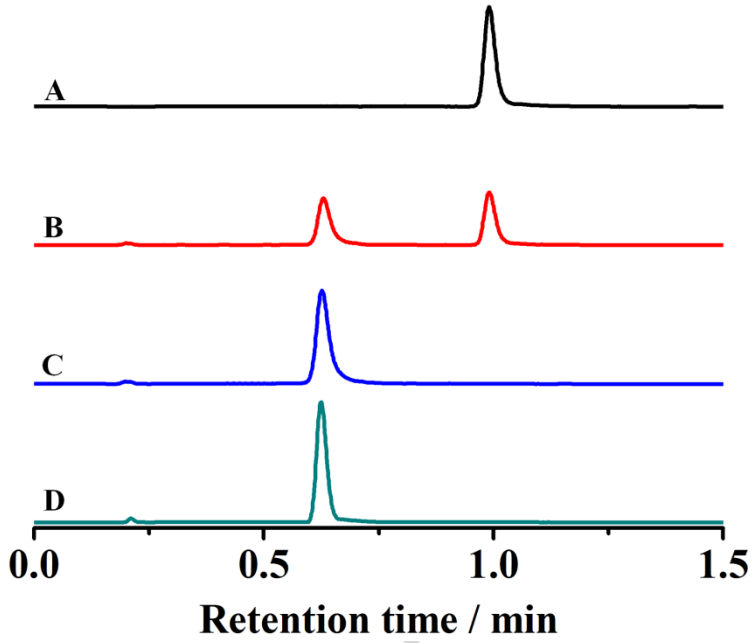


Fig. 4 HPLC chromatograms of probe **1**, **1**+N_2H_4 and compound **2** (Sample A: probe **1** only; Sample B: probe **1** + 5 equiv N_2H_4; Sample C: probe **1** + 20 equiv N_2H_4; Sample D: compound **2** only).

3.5. Theoretical calculation

To get further insight into the relationship between the structural changes and optical response of probe **1** to hydrazine, a theoretical calculation was carried out by Density Functional Theory (DFT) with the B3LYP/6-31+G(d,p) method basis set using the Gaussian 09 program. The optimized geometries and the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of probe **1** and compound **2** are presented in Fig. 5. Compond **2** has conjugated π-electrons and a push-pull electronic structure, phenol as the donor and TCF as the acceptor. Due to the presence of electron-withdrawing group, acetyl, coupled on phenolic hydroxyl

group, probe **1** has lowered electron density localized on the extended π-conjugate system and the silenced ICT progress. Upon the addition of hydrazine, probe **1** transformed into compound **2**, which enables an ICT from the activated phenolate ion to the acceptor and the formed push-pull conjugated structural possesses strong fluorescence emission. The energy gaps between the HOMO and LUMO of were calculated to 3.67 and 2.99 eV for **1** and **2**, respectively. The red shift absorption spectrum of the probe can be attributed to the enlarged energy gap.

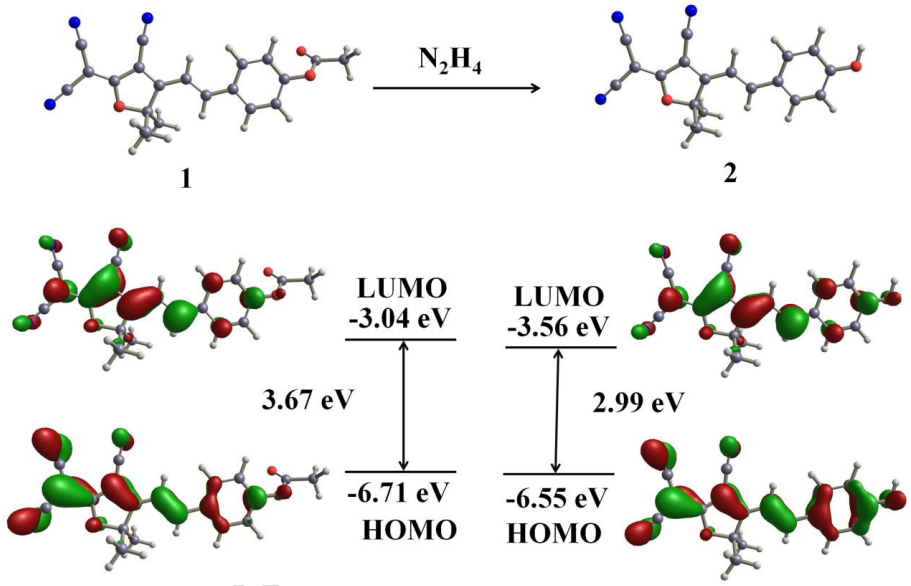


Fig. 5 Energy diagrams of optimized geometries, HOMO and LOMO orbitals of **1** and **2** calculated at the DFT level using a B3LYP/6-31+G(d,p) basis set.

3.6. Application in water sample

Hydrazine is highly toxic and has been widely used in various industrial processes. Thus, detection of hydrazine in real samples is of great importance. To explore the practical applications, probe **1** was applied to monitoring hydrazine in tap water. The results showed satisfactory recoveries (from 97.6% to 108%) and analytical precision

(R.S.D≤7.4%), which confirmed the feasibility and reliability of the proposed probe for hydrazine detection (Table S2).

3.7. Cellular imaging

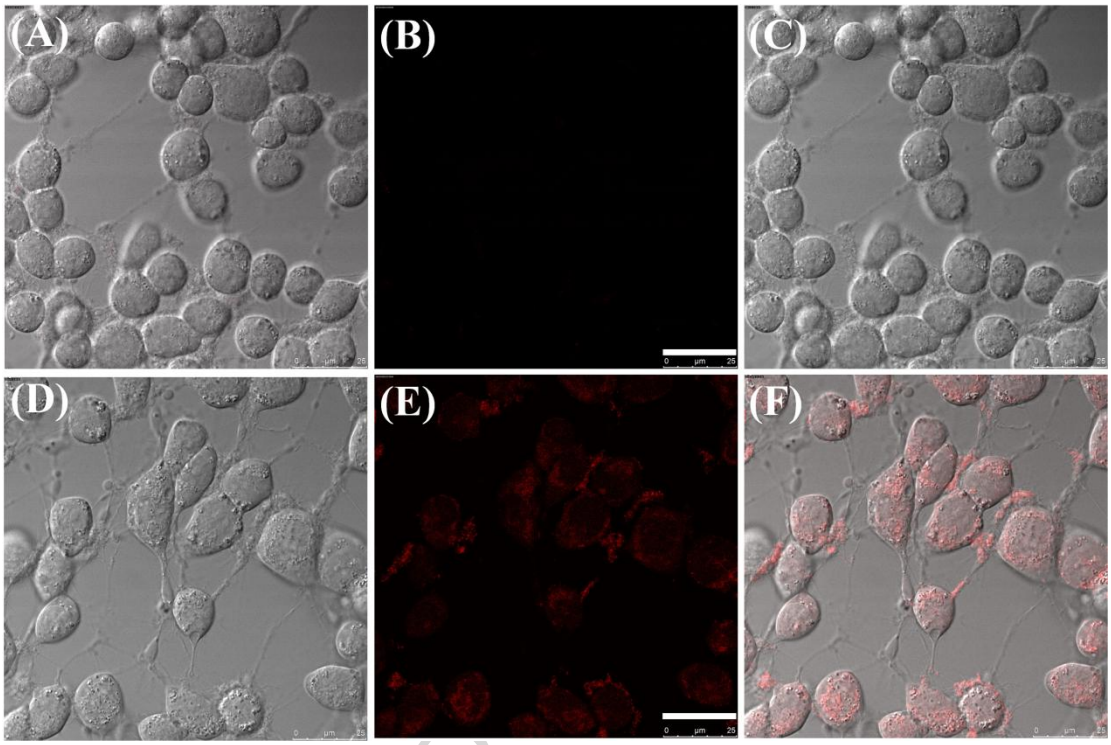


Fig. 6 Confocal fluorescence images of HeLa cells: Cells incubated with probe **1** (20 μM) for 1 h (A–C); image of cells after treatment with probe **1** (10 μM) for 1 h and subsequent treatment of the cells with 100 μM hydrazine for 1 h (D–F). (A and D) Bright-field images; (B and E) red channel; (C and F) Merged images. λ_{ex} = 580 nm, scare bar = 50 μm.

To further investigate the potential application of HFP in living system, probe **1** was used to visualize hydrazine in live cell. Hela cells were incubated with probe **1** (10 μM) alone showed no intracellular fluorescence under the selective excitation at 580 nm (Fig. 6B). The cells, which were incubated with **1** (10 μM) for 1 h and consequently with hydrazine (50 μM) for an additional 1 h, displayed strong red

fluorescent emission (Fig. 6E). The results indicated that probe **1** was living cell membrane permeable, and can be utilized for monitoring hydrazine in living cells. Additionally, the cytotoxicities of probe **1** towards different types of cells were evaluated using MTT assay. All these inspected cells remained in good condition upon treatment with 0-20 μM of **1** for as long as 24 h (Fig. S6), which demonstrated the excellent biocompatibility of the probe.

4. Conclusion

In summary, we developed a turn-on long-wavelength fluorescent probe for hydrazine by using tricyanofuran-based D-π-A system as the fluorophore and acetyl group as the recognizing moiety. The presence of hydrazine resulted in large red-shift in absorption spectrum and significant enhancement in fluorescence emission of the probe solution through cleaving the acetyl group and releasing the phenolic hydroxyl group. The sensing mechanism was confirmed by HPLC, MS, UV-vis and emission spectroscopic studies. The probe **1** exhibited high selectivity for hydrazine and a low LOD of 0.16 μM. Moreover, the probe can be utilized for practical detection of hydrazine in water samples as well as in living cells.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

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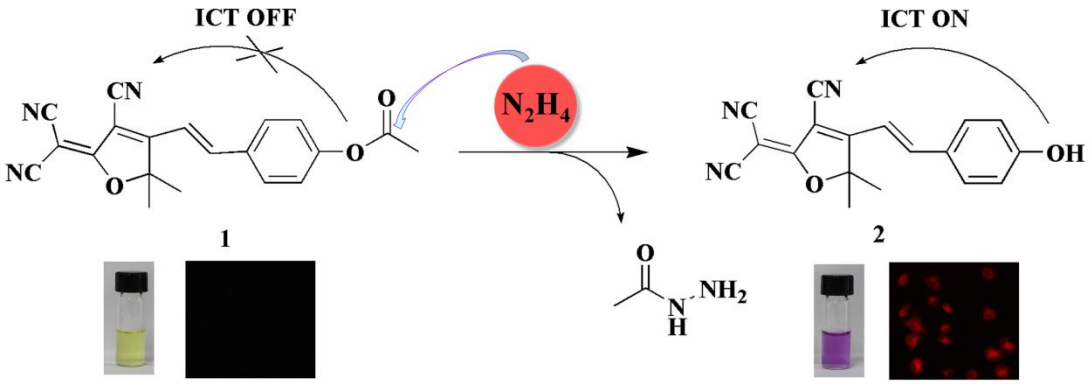
Graphical abstract



Hightlights

- A highly selective long-wavelength turn-on fluorescent probe has been developed for the detection of N_2H_4.
- The probe is highly sensitive towards N_2H_4 (LOD: 0.16 μM).
- The probe was readily utilized for the detection of hydrazine in living cells.