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Novel pyrazoline-based selective fluorescent probe for the detection of hydrazine

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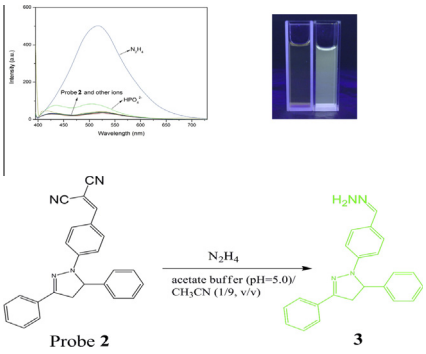
HIGHLIGHTS

- Design and synthesize a novel pyrazoline-based fluorescent probe for the detection of hydrazine.
- The probe is of high selectivity and has low detection limit.
- The probe can work over a pH range of 5.0–8.0.
- The probe has long emission wavelength (520 nm) and a large stokes shift (~140 nm).

GRAPHICAL ABSTRACT

Hydrazine is a very toxic material widely used in industry. A novel pyrazoline-based fluorescent probe with a simple structure and low detection limit for the detection of hydrazine is designed and synthesized. The probe can respond selectively to hydrazine over other molecules with marked fluorescence enhancement.



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ABSTRACT

A novel pyrazoline-based fluorescent probe, 2-[4-(3,5-diphenyl-4,5-dihydro-pyrazol-1-yl)-benzylidene]-malononitrile, with a simple structure and low detection limit (6.16×10^{-6} M) for the detection of hydrazine is designed and synthesized. The probe responds selectively to hydrazine over other molecules with marked fluorescence enhancement. The probe can detect hydrazine effectively at pH 5.0–9.0 with a special emission wavelength at 520 nm. Moreover, the probe can be used to detect hydrazine from variety of natural source water.

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Introduction

Hydrazine (N_2H_4), because of its high activity and strong basicity, is widely used as an important reactant in the synthesis of many chemicals including pharmaceuticals, pesticides, photography chemicals, emulsifiers and dyes [1–4]. In addition, hydrazine always plays an important part in propulsion systems and hydrazine fuel cells as a highly explosive fuel [5–8]. In industry, hydrazine has been used as blowing agent, antioxidant, anti-corrosion agent and fuel [9]. At the same time, hydrazine is a model toxin and easily absorbed by oral, dermal and inhalation uptake leading to various organs and system damage [10–12], especially for nervous system [3]. Actually, hydrazine has been classified as a

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probable human carcinogen by the U.S. Environmental Protection Agency (EPA) with an exposure limit of 10 ppb [12]. Therefore, developing new detection methods of hydrazine has attracted much attention.

Up till present, all kinds of chemical detection methods of hydrazine have been developed including chemiluminescence [13], chromatography–mass spectrometric [14], titrimetric [15], electrochemical methods [16]. There is no exception that the above methods require expensive experimental equipment, tedious operation processes or long time. By reason of the high sensitivity and selectivity, the fluorescent chemosensor is a convenient and practical way to detect important small molecules, but only a few fluorescent probes for hydrazine have been reported. In these reports, malononitrile group [17–21], aliphatic group [22–29], trifluoroacetylacetone group [30,31], phthalimide group [32,33] and aldehyde group [34] are chosen as the sensing part to detect hydrazine, and have achieved good results. Nevertheless, poor selectivity, strong background signals, narrow measurement range and high detection limit still remain to be improved.

We designed and synthesized a new pyrazoline-based selective fluorescent probe for the detection of hydrazine with high selectivity, proper pH range. To the best of our knowledge, there are few pyrazoline-based selective fluorescent probes for the detection of hydrazine, and the probe we designed inherits the features from pyrazoline with strong fluorescence, simple synthesis and so on [35–37]. What is more, the emission length of the probe is at 520 nm, which is of great difference from other common pyrazoline-based fluorescent probes [38–41]. Because of its long emission wavelength (520 nm) and a large stokes shift (~140 nm), the probe avoids most of the background influence. The probe should have a wide and strong applicability.

Material and methods

General information and materials

Thin-layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (300 MHz and 75 MHz) spectrometer, using DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on an XD-4 digital micro melting point apparatus. IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were recorded on a Q-TOF6510 spectrograph (Agilent). UV–vis spectra were recorded on a U-4100 (Hitachi). Fluorescent measurements were recorded on a Perkin–Elmer LS-55 luminescence spectrophotometer. All pH measurements were made with a Model PHS-3C pH meter (Shanghai, China) and operated at room temperature about 298 K. 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 $Ca(NO_3)_2{\cdot}4H_2O$, $NaNO_3$, $AgNO_3$, $Ba(NO_3)_2$, $Cd(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, NaBr, CH_3COONa, NaCl, $NaH_2PO_4{\cdot}2H_2O$, $NaHCO_3$, $Na_2HPO_4{\cdot}7H_2O$, $NaHSO_4$, NaI, $Na_2SO_3{\cdot}7H_2O$, Na_2SO_4.

Synthesis

*Synthesis of 2-[4-(3,5-diphenyl-4,5-dihydro-pyrazol-1-yl)-benzylidene]-malononitrile (probe **2**)*

According to the literature [42], compound **1** was easily prepared in 40% yield. Compound **1** (0.342 g, 1.05 mmol), malononitrile (0.069 g, 1.05 mmol), EtOH (20 mL) were added to a flask. After added 3 drops of piperidine, the mixture was heated to reflux for 2 h. The precipitate was isolated and was recrystallized from EtOH to obtain purplish-brown solid (probe **2**) in 58.8% yield (0.231 g). M.P. 231–233 °C; IR (KBr, cm^{-1}): 3059, 2920, 2217, 1604; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.28 (dd, 1H, J = 18.0, 4.5 Hz, 4-H_{trans}), 4.05 (dd, 1H, J = 12.0, 18.0 Hz, 4-H_{cis}), 5.75 (dd, 1H, J = 4.5, 12.0 Hz, 5-H of pyrazoline), 7.15 (d, 2H, J = 12.0 Hz, Ar—H), 7.25–7.39 (m, 5H, Ar—H), 7.47 (dd, 3H, J = 4.8, 1.5 Hz, Ar—H), 7.80–7.87 (m, 4H, Ar—H), 8.09 (s, 1H, =*CH*); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.15, 153.09, 147.80, 141.09, 133.26, 131.16, 130.04, 129.20, 128.78, 127.83, 126.56, 125.65, 121.37, 115.73, 114.91, 112.85, 71.47, 62.11, 43.03 ppm; HRMS: calcd for $[M+H]^+$ $C_{25}H_{19}N_4$: 375.1610; found: 375.1552.

*Synthesis of adduct (**3**) of probe **2** and hydrazine*

Probe **2** (52 mg) was mixed with two equivalents hydrazine in acetonitrile and reacted for 24 h at room temperature. Then, the solution was poured into water and after work-up a yellow solid product (**3**) was obtained (35 mg). IR (KBr, cm^{-1}): 3384, 3029, 2901, 1602; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.12 (dd, 1H, J = 18.0, 6.0 Hz, 4-H_{trans}), 3.93 (dd, 1H, J = 12.0, 18.0 Hz, 4-H_{cis}), 5.52 (dd, 1H, J = 6.0, 12.0 Hz, 5-H of pyrazoline), 6.37 (s, 2H, NH_2), 6.97 (d, 2H, J = 8.7 Hz, Ar—H), 7.23–7.46 (m, 10H, Ar—H), 7.57 (s, 1H, =*CH*), 7.75 (dd, 2H, J = 1.5, 8.1 Hz, Ar—H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 147.56, 143.51, 142.38, 139.26, 132.15, 128.98, 128.74, 128.63, 127.42, 127.03, 126.10, 125.79, 125.71, 112.88, 62.96, 42.93 ppm; HRMS: calcd for $[M+H]^+$ $C_{22}H_{21}N_4$: 341.1766; found: 341.1724.

Spectroscopic data

A 1.0×10^{-3} M of stock solution of probe **2** was prepared in acetonitrile. The cationic (Ag^+, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Hg^{2+}, Mg^{2+}, Na^+, Pb^{2+}), anion (Br^-, $CH_3CO_2^-$, Cl^-, $H_2PO_4^-$, HCO_3^-, HPO_4^{2-}, HSO_4^-, I^-, NO_3^-, SO_3^{2-}, SO_4^{2-}) and hydrazine stocks were all in deionized water with a concentration of 10^{-2} M for UV–vis absorption and fluorescence spectra. For all measurements of fluorescence spectra, excitation was at 380 nm with 12.5 nm of excitation slit width and scan speed was set at 600 nm × min^{-1}. All UV–vis and fluorescence titration experiments were carried out using 10 μM of probe **2** in the mixture solvent (CH_3CN/acetate buffer, v/v = 9:1, pH = 5.0) with varying concentrations of analytes at room temperature after 24 h, respectively.

Fluorescence quantum yield

The ability for the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). Quantum yield was determined by the relative comparison procedure, using quinine sulfate dehydrate (⩾99.0%) in 0.1 N H_2SO_4 as the main standard. The corrected emission spectra were measured for the quinine sulfate dehydrate standard (λ_{ex} = 380 nm; A (Absorption) < 0.01; Φ_F = 0.51) [43]. For all the measurements of fluorescence spectra, scan speed was 600 nm × min^{-1} using a quartz cell of 1 cm optical path length. The UV–vis absorption spectra were recorded in a standard 1 cm path length quartz cell in range 390–750 nm with spectral resolution 1 nm. The general equation used in the determination of relative quantum yields from earlier research was given in Eq. (1) [44].

$$\Phi_F = (\Phi_{FS})(FAu)(As)(\eta_u^2)/(FAs)(Au)(\eta_s^2) \quad (1)$$

where Φ_F and FA are fluorescence quantum yield and integrated area under the corrected emission spectra, respectively; A is absorbance at the excitation wavelength; η represents the refractive index of the solution; and the subscripts u and s refer to the unknown and the standard, respectively.

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