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Colorimetric and fluorescent detection of hydrazine with high sensitivity and excellent selectivity

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Abstract

It is critical to develop probes for rapid, selective, and sensitive detection of the highly toxic hydrazine in both environmental and biological science. In this work, under mild condition, a novel colorimetric and off-on fluorescent probe was synthesized for rapid recognition of hydrazine with excellent selectivity over other various species including some biological species, metal ions and anions. The limit of quantification (LOQ) value was 1.5×10^{-4} M–3.2×10^{-3} M (colorimetric method) and 1.5×10^{-4} M−3.2×10^{-3} M (fluorescent method) with as low as detection limit of 46.2 μM.

Keywords: Colorimetric; Off-on fluorescent probe, Quantitative detection; Hydrazine; Naked-eye detection

Introduction

As a highly reactive base and reducing agent, hydrazine plays crucial roles in many fields such as the chemical, pharmaceutical and agricultural industries [1−3]. Hydrazine is also a high-energy fuel for rocket-propulsion systems and missile systems due to its detonable characteristics [4,5]. However, as a class of highly toxic and pollutant compound, hydrazine can potentially lead to serious environmental contamination during its manufacture, use, transport and disposal. In addition, as a neurotoxin, hydrazine has several mutagenic effects, which can cause damage to the liver, lungs, kidneys and human central nervous system [6,7]. As a result, hydrazine has been classified as a probable human carcinogen by the U.S. Environmental Protection Agency and has a low threshold limit value of 10 ppb [8]. Therefore, an efficient and simple method for determining hydrazine level is therefore urgently needed in both environmental and biological science.

In recent years, the development of small molecular fluorescent probes toward metal ions, anions and biomolecules has attracted great attention due to their simplicity, high sensitivity, and instantaneous response [9−15]. However, available fluorescent probes for hydrazine are still very limited [16−20].

In general, fluorescent probes depend on emission intensity or position power and detector sensitivity, while color changes based on absorption properties of the ground state are more suitable for direct observation with the naked eye [21,22], and considerable efforts have been devoted to designing colorimetric probes toward hydrazine during the past few decades [23−31]. Therefore, it is still meaningful to prepare colorimetric and fluorescent probes for hydrazine.

Using 1,8-naphthalimide unit as useful fluorophores, we have designed and synthesized several 1,8-naphthalimide-based colorimetric and fluorescent probes because the photophysical properties are easily influenced by reagents [32,33]. Based on photo-induced electron transfer (PET) mechanism, a few 4-substituted 1,8-naphthalimide-based fluorescent off-on probes have been recently reported [34−36]. These observations encouraged us to make use of such PET process to design hydrazine-responsive fluorescent probes based on 1,8-naphthalimide derivatives.

In this paper, based on 1,8-naphthalimide, selective colorimetric and fluorescent probe **1** (**Scheme S1**) was synthesized. Probe **1** can quantitatively detect hydrazine with both great color and fluorescence change in solution. The detection limit on UV-vis response of the sensor can be as low as 74.5 nM. Further studies demonstrate that this probe has good sensitivity and selectivity.

Experimental

Methods and materials

4-Bromo-1,8-naphthalic anhydride, monoethanolamine, glacial acetic acid, ethanol, 2-methoxyethanol, 80% hydrazine hydrate, triethylamine, phthalic anhydride, KCl, NaCl, $MgCl_2$, $Al(NO_3)_3$, $CaCl_2$, $Cd(NO_3)_2$, $MnCl_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $ZnCl_2$, $Hg(NO_3)_2$, $AgNO_3$, $Fe(NO_3)_3$, $CuCl_2$, and $PbCl_2$, NaBr, NaCl, $NaNO_3$, Na_2SO_3, Na_2SO_4, $NaClO_3$, $NaClO_4$, $NaHSO_3$, $NaHSO_4$, NaH_2PO_4, Cys, Phe, Gly, His, Tyr, Pro, Ser, Thr, Val, Trp, Asp, Glu, and $SOCl_2$. All chemicals and solvents were analytical grade except 2-methoxyethanol (chemical grade) and used without further purification. Compounds **3** and **2** and **1** were synthesized by following **Scheme S1**. Compounds **3** and **2** have ever

been synthesized and reported by us and here were synthesized according to our reported method [33].

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 NMR spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane (TMS) as the internal standard. Elemental analysis data were obtained on Automatic Element Analyzer.

All spectral characterizations were carried out in HPLC-grade solvents at 20°C within a 10 mm quartz cell. UV-vis absorption spectra were measured with a TU-1901 double-beam UV-vis spectrophotometer. Fluorescence spectroscopy was determined on a Hitachi F-4600 spectrometer.

*Synthesis of Probe **1***

Compound **2** (0.2713 g, 1 mmol) and phthalic anhydride (0.1852 g, 1.25 mmol) were dissolved in 50 mL glacial acetic acid. The mixture was refluxed for 5 h, and then cooled to room temperature. After filtration of the above mixture, the crude product was obtained as yellow solid. The final product (296.3 mg, 73.0%) was obtained by washing the crude product with glacial acetic acid three times. ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ_H 4.29 (t, 4H), 7.02 (d, 1H), 7.89 (t, 1H), 8.03 (m, 4H), 8.26 (d, 1H), 8.52 (d, 1H), 8.72 (d, 1H), 10.21 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 170.8, 166.3, 164.2, 163.43, 148.8, 135.8, 133.7, 131.6, 130.0, 129.3, 128.8, 126.3, 124.4, 122.5, 119.6, 113.1, 106.4, 61.5, 21.0. Elemental analysis calcd. for $C_{22}H_{15}N_3O_5$, C: 65.83%; N: 10.47%; H: 3.77%; found, C: 65.374%; N: 9.982%; H: 3.738%.

Results and Discussion

*Synthesis of probe **1***

In this work, the probe **1** was synthesized via three-step synthetic procedure starting from 4-bromo-1,8-naphthalic anhydride. The reaction of compound 4-bromo-1,8-naphthalic anhydride with monoethanolamine in ethanol gave the product **3** in a 88.8% yield. Compound **3** reacted with 80% hydrazine hydrate in 2-methoxyethanol and gave compound **2** in an 89.7% yield. The probe **1** was obtained in a 73.0% yield by the reaction of compound **2** with phthalic anhydride in glacial acetic acid. The chemical structures were confirmed by ^{1}H, ^{13}C NMR, and elemental analysis.

*Hydrazine hydrate colorimetric sensing properties of probe **1** in solution*

To investigate the changes in absorption spectrum of probe **1** upon exposure to hydrazine hydrate, UV-vis titration experiments were conducted with hydrazine hydrate in solution of **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) (**Fig. 1a**). As is evident from inspection of **Fig. 1a**, probe **1** exhibits no absorption at 520 nm in solution in the absence of hydrazine hydrate. However, upon addition of hydrazine hydrate, a significant increase in the absorption peak at 520 nm was very quickly (several seconds) observed with the original peak at 400 nm decreasing. Meanwhile, two clear isosbestic points were observed at 358 and 444 nm respectively, indicating that only one product was generated from 1 upon the reaction to hydrazine. **Fig. S1** (Supporting Information) indicates the relationship between the absorbance ratio A_{520}/A_{400} (A_{520} and A_{400} mean the absorbance at 520 nm and 400 nm respectively) and the concentration of hydrazine hydrate. In the concentration range of 1.5×10^{-4} M and 13.2×10^{-3} M, the absorbance ratio A_{520}/A_{400} of **1** is in good linear relationship with hydrazine hydrate concentration (**Fig. 1b**), implying that hydrazine hydrate can be quantitatively detected in a wider

concentration range. At the same time, the solution color changed from colorless to pink (**Fig. 1c**), implying that probe **1** can be a naked-eye probe toward hydrazine hydrate. These results led us to conclude that **1** could be an effective colorimetric probe for hydrazine hydrate. The proposed sensing mechanism was shown in **Scheme 1**.

(**Insert: Fig. 1**)

(**Insert: Scheme 1**)

*Hydrazine hydrate fluorescent sensing properties of **1** in solution*

After standing for 24 hours, the color of the above prepared solutions of probe **1** containing different concentration of hydrazine (tested in colorimetric sensing experiments) changed colorless, indicating new chemical change happened in the solution. Upon excitation at 440 nm on these solutions, the emission intensity at 540 nm gradually increased with increased hydrazine concentration (**Fig 2a**). **Fig. S2** (Supporting Information) indicates the relationship between the fluorescence intensity at 540 nm and the concentration of hydrazine hydrate. In the range between 1.5×10^{-4} M and 3.2×10^{-3} M, a good linear relationship between the fluorescence peak intensity with hydrazine concentration was obtained (**Fig. 2b**), implying that hydrazine can be quantitatively detected in a wider concentration range both with UV-vis and fluorescence spectroscopy. From the linear calibration graph with the fluorescence titration experiment, the detection limit of probe **1** for hydrazine was found to be about 46.2 μM based on signal-to-noise ratio (S/N) = 3 [36, 37], which was sufficiently low for the detection of hydrazine. **Fig 2c** demonstrates the fluorescence of the above solutions change. These results led us to conclude that **1** could be an effective colorimetric and fluorescent off-on probe for hydrazine.

(**Insert: Fig. 2**)

Sensing mechanism

As illustrated in **Fig. 1**, upon addition of hydrazine hydrate and within several seconds, a new absorption band centered at 520 nm appeared and increased with the original peak at 400 nm decreasing, and then the peak at 520 nm gradually disappeared. This process is so fast that it is difficult to study this colorimetric sensing mechanism, and we propose that such absorption spectra change may be ascribed to the formation of compound **4** (**Scheme 1**). The fluorescent sensing mechanism was studied by Mass spectra. Whilst on reaction of hydrazine, one peak appeared at m/z = 227 corresponding to the species [2+3H]. Such Mass spectra data confirm that compound **2** was formed through the reaction of hydrazine with probe **1** (**Scheme 1**).

*Selectivity sensing of **1** toward hydrazine*

To evaluate the selectivity of probe **1** for hydrazine, various species including environmentally and biologically relevant biomolecules, metal ions and anions were tested. As shown in Figures **3, 4, 5,** and **6**, only the introduction of hydrazine to the probe **1** solution induced a significant enhancement in the absorption at 520 nm, a great color change from colorless to pink, and a great fluorescence intensity increase at 540 nm. In the same condition, other tested species mentioned above did not induce any UV-vis and fluorescence spectroscopic change to the probe **1** solution, indicating that probe **1** as a probe have high selectivity toward hydrazine over many common organic amine molecules, biomolecules, metal ions and anions.

(**Insert: Fig. 3**)

(**Insert: Fig. 4**)

(**Insert: Fig. 5**)

(**Insert: Fig. 6**)

Conclusion

Based on 1,8-naphthalimide, a novel colorimetric and off-on fluorescent probe for hydrazine has been developed with high selectivity over various environmentally and biologically relevant molecules, metal ions and anions. With colorimetric method, the probe can detect hydrazine with a distinct color change from colorless to pink in very fast response time (<1 min), and can detect hydrazine quantitatively in the concentration range from 1.5×10^{-4} M to 3.2×10^{-3} M. In addition, the probe can also detect hydrazine quantitatively in the concentration range from 1.5×10^{-4} M to 3.2×10^{-3} M with a LOD of 46.2 μM with an off-on fluorescent mode.

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Figure Captions

Scheme 1 Proposed sensing mechanism of probe **1** toward hydrazine.

Fig. 1 a) Absorption spectra change of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) upon addition of hydrazine hydrate (0.01 M, water). b) Absorption spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) as a linear dependence with the concentration of hydrazine hydrate. A_{520} and A_{400} represent the absorbance at 520 nm and 400 nm respectively. c) photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of hydrazine hydrate (the concentrations from left to right are 0, 3.0×10^{-5} M, 9.0×10^{-5} M, 1.5×10^{-4} M, 2.1×10^{-4} M, 3.0×10^{-4} M, 4.5×10^{-4} M, 6.0×10^{-4} M, 7.5×10^{-4} M, 9.0×10^{-4} M, 1.05×10^{-3} M, 1.2×10^{-3} M, 1.35×10^{-3} M, 1.65×10^{-3} M, 1.8×10^{-3} M) in daylight.

Fig. 2 a) Emission spectra change of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) upon addition of hydrazine hydrate (0.1 M, water). b) Emission spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) as a linear dependence with the concentration of hydrazine hydrate. I_{540} represent the emission intensity at 540 nm. c) photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of hydrazine hydrate (the concentrations from left to right are 0, 3.0×10^{-5} M, 9.0×10^{-5} M, 1.5×10^{-4} M, 2.1×10^{-4} M, 3.0×10^{-4} M, 4.5×10^{-4} M, 6.0×10^{-4} M, 7.5×10^{-4} M, 9.0×10^{-4} M, 1.05×10^{-3} M, 1.2×10^{-3} M, 1.35×10^{-3} M, 1.5×10^{-3} M, 1.8×10^{-3} M) under a UV lamp (365 nm). The reaction time is 24 hours.

Fig. 3 Absorption (a) and emission (b) spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different organic amine molecules (1.8×10^{-3} M). The organic amine molecules used were methylamine, 1,2-ethylenediamine, aniline, toluidine, trimethylamine, and 1,4-diaminobenzene. The excitation wavelength was 440 nm

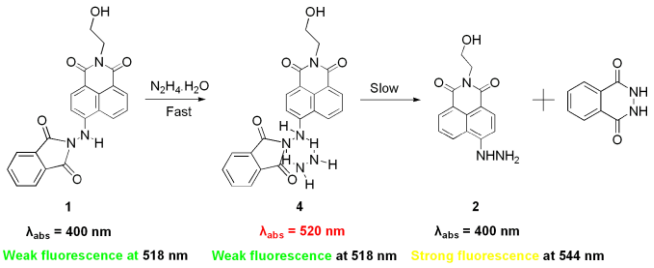
and the reaction time was 24 hours.

Fig. 4 Absorption (a) and emission (b) spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different biomolecules (1.8×10^{-3} M). The biomolecules used were Cys, Gly, Met, Tyr, Pro, Ser, Thr, Val, His, Glc, Trp, and Asp. The excitation wavelength was 440 nm and the reaction time was 24 hours. photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in daylight (c) and under a UV lamp (365 nm) (d) in the presence of 60 eq different species (From left to right: only probe **1**, hydrazine hydrate, Cys, Gly, Met, Tyr, Pro, Ser, Thr, Val, His, Glc, Trp, and Asp.

Fig. 5 (a) absorption spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different metal ions (1.8×10^{-3} M). The metal ions used were Ca^{2+}, Cd^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Ag^{+}, and Pb^{2+}. (b) Emission spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different metal ions (1.8×10^{-3} M). The metal ions used were Ca^{2+}, Cd^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Ag^{+}, Fe^{3+}, Cu^{2+}, and Pb^{2+}. The reaction time was 24 hours and the excitation wavelength was 440 nm. photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in daylight (c) and under a UV lamp (365 nm) (d) in the presence of 60 equiv. different species (From left to right: only probe **1**, hydrazine hydrate, Ca^{2+}, Cd^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, and Zn^{2+}).

Fig. 6 Absorption (a) and emission (b) spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different anions (1.8×10^{-3} M). The anions used were Br^{-}, Cl^{-}, NO_3^{-}, SO_3^{2-}, SO_4^{2-}, ClO_3^{-}, $H_2PO_4^{-}$, HSO_3^{-}, and HSO_4^{-}. The reaction time was 24 hours and the excitation wavelength was 440 nm. Photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in daylight (c) and under a UV lamp (365 nm) (d) in the presence of 60 eq different species (From left to right: only probe **1**, hydrazine hydrate,

Br^-, Cl^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, ClO_3^-, $H_2PO_4^-$, HSO_3^-, and HSO_4^-).



Scheme 1 Proposed sensing mechanism of probe **1** toward hydrazine.

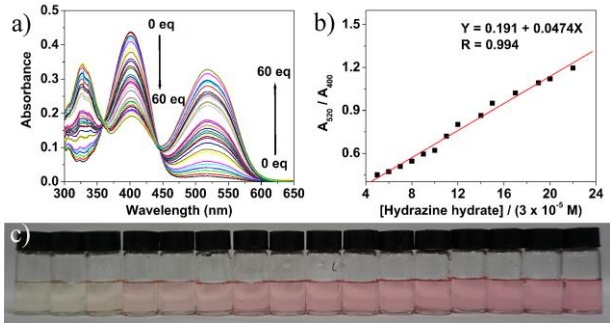


Fig. 1 a) Absorption spectra change of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) upon addition of hydrazine hydrate (0.01 M, water). b) Absorption spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) as a linear dependence with the concentration of hydrazine hydrate. A_{520} and A_{400} represent the absorbance at 520 nm and 400 nm respectively. c) photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of hydrazine hydrate (the concentrations from left to right are 0, 3.0×10^{-5} M, 9.0×10^{-5} M, 1.5×10^{-4} M, 2.1×10^{-4} M, 3.0×10^{-4} M, 4.5×10^{-4} M, 6.0×10^{-4} M, 7.5×10^{-4} M, 9.0×10^{-4} M, 1.05×10^{-3} M, 1.2×10^{-3} M, 1.35×10^{-3} M, 1.65×10^{-3} M, 1.8×10^{-3} M) in daylight.

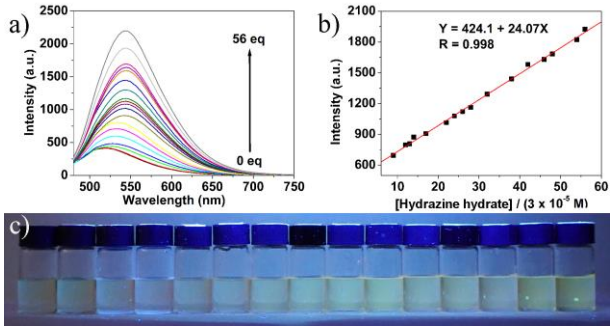


Fig. 2 a) Emission spectra change of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) upon addition of hydrazine hydrate (0.1 M, water) with the excitation at 440 nm. b) Emission spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) as a linear dependence with the concentration of hydrazine hydrate. I_{540} represent the emission intensity at 540 nm. c) photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of hydrazine hydrate (the concentrations from left to right are 0, 3.0×10^{-5} M, 9.0×10^{-5} M, 1.5×10^{-4} M, 2.1×10^{-4} M, 3.0×10^{-4} M, 4.5×10^{-4} M, 6.0×10^{-4} M, 7.5×10^{-4} M, 9.0×10^{-4} M, 1.05×10^{-3} M, 1.2×10^{-3} M, 1.35×10^{-3} M, 1.5×10^{-3} M, 1.8×10^{-3} M) under a UV lamp (365 nm). The reaction time is 24 hours.

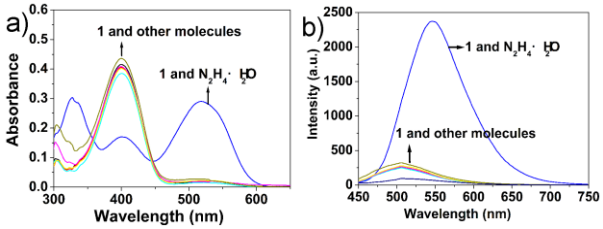


Fig. 3 Absorption (a) and emission (b) spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different organic amine molecules (1.8×10^{-3} M). The organic amine molecules used were methylamine, 1,2-ethylenediamine, aniline, toluidine, trimethylamine, and 1,4-diaminobenzene. The excitation wavelength was 440 nm and the reaction time was 24 hours.

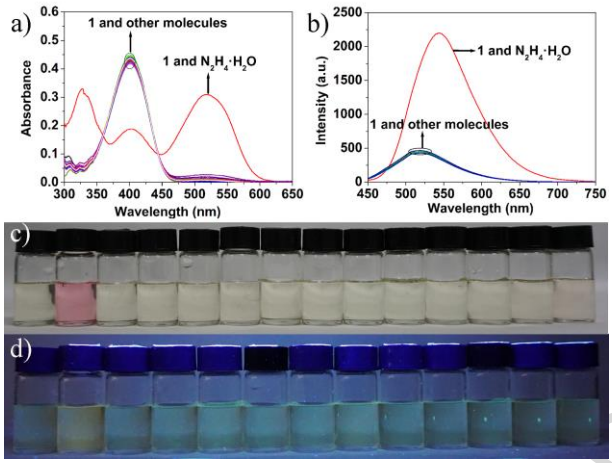


Fig. 4 Absorption (a) and emission (b) spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different biomolecules (1.8×10^{-3} M). The biomolecules used were Cys, Gly, Met, Tyr, Pro, Ser, Thr, Val, His, Glc, Trp, and Asp. The excitation wavelength was 440 nm and the reaction time was 24 hours. photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in daylight (c) and under a UV lamp (365 nm) (d) in the presence of 60 eq different species (From left to right: only probe **1**, hydrazine hydrate, Cys, Gly, Met, Tyr, Pro, Ser, Thr, Val, His, Glc, Trp, and Asp.

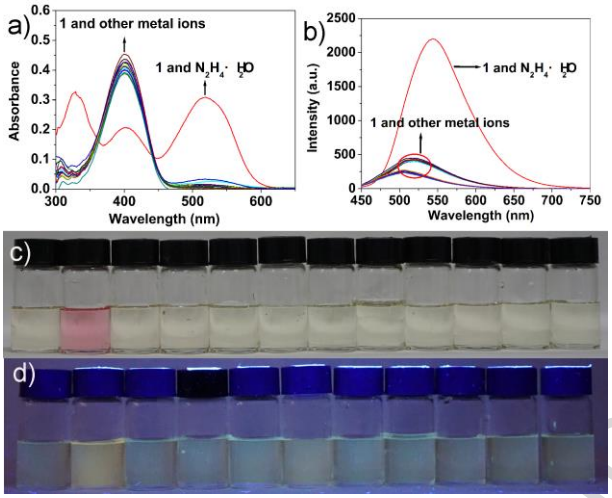


Fig. 5 (a) absorption spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different metal ions (1.8×10^{-3} M). The metal ions used were Ca^{2+}, Cd^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Zn^{2+} Hg^{2+}, Ag^{+}, and Pb^{2+}. (b) Emission spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different metal ions (1.8×10^{-3} M). The metal ions used were Ca^{2+}, Cd^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Zn^{2+} Hg^{2+}, Ag^{+}, Fe^{3+}, Cu^{2+}, and Pb^{2+}. The reaction time was 24 hours and the excitation wavelength was 440 nm. photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in daylight (c) and under a UV lamp (365 nm) (d) in the presence of 60 equiv. different species (From left to right: only probe **1**, hydrazine hydrate, Ca^{2+}, Cd^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, and Zn^{2+}).

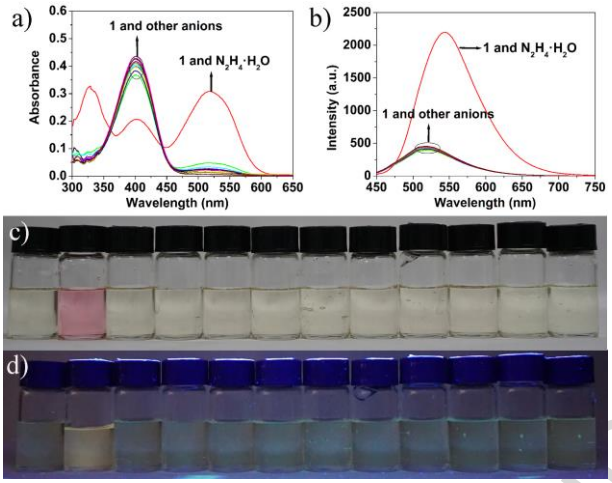
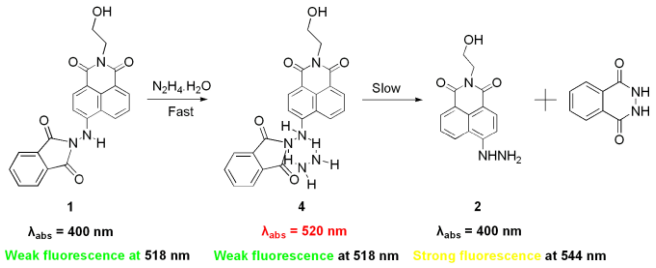


Fig. 6 Absorption (a) and emission (b) spectra response of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in the presence of different anions (1.8×10^{-3} M). The anions used were Br^-, Cl^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, ClO_3^-, $H_2PO_4^-$, HSO_3^-, and HSO_4^-. The reaction time was 24 hours and the excitation wavelength was 440 nm. Photographs of probe **1** (3.0×10^{-5} M, DMSO/PBS = 9:1, v/v) in daylight (c) and under a UV lamp (365 nm) (d) in the presence of 60 eq different species (From left to right: only probe **1**, hydrazine hydrate, Br^-, Cl^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, ClO_3^-, $H_2PO_4^-$, HSO_3^-, and HSO_4^-).



Graphical Abstract

Based on 1,8-naphthalimide, a novel colorimetric and off-on fluorescent probe for hydrazine has been developed with high selectivity over various environmentally and biologically relevant molecules, metal ions and anions.

Highlights

►A hydrazine-responsive colorimetric and fluorescent probe has been developed.

►The probe can quantitatively detect hydrazine with great color and fluorescence change.

►The probe showed high selectivity and sensitivity toward hydrazine.