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# A novel berberine-based colorimetric and fluorimetric probe for hydrazine detection

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Hydrazine in water and soil has caused a serious disease threatening human health. It is critical to develop a simple and effective method for hydrazine detection. In this work, a simple fluorescent probe (BP) for hydrazine detection was synthesized from berberine. The probe has short synthesis route (2 steps), low detection limit (1.37 µM), excellent fluorescence properties and convenient naked-eye detection. In addition, BP displayed excellent selectivity and specificity over other metal ions, anions and amines. Moreover, BP was also successfully used to detect hydrazine gas at different concentrations.

# 1 Introduction

As one of important chemical materials, hydrazine (N<sub>2</sub>H<sub>4</sub>) has been widely used in various industries, chemical, pharmaceutical, agricultural, military and aerospace.1-5 But it has caused great concern on human health<sup>6,7</sup> and environmental pollution problems<sup>8,9</sup> because of its highly toxicity, mutagenic, carcinogenic and absorbent.<sup>10</sup> According to the regulation of U.S. Environmental Protection Agency (USEPA) in 1999, hydrazine's threshold limit value (TLV) is 10 ppb.<sup>11</sup> Therefore, developing an effective method to detect hydrazine is an important for environment and human healthy.

In the last decade, hydrazine can be routinely analyzed by many chemical analytical methods such as electrochemical analysis,12 liquid chromatograph,13 mass spectrometric,14 colorimetry,15 gas chromatography<sup>16</sup> and titrimetry.<sup>17</sup> However, most of these conventional techniques have many disadvantages, such as time consuming, complicated experimental processing and destructive for cells.<sup>18</sup> Recently, fluorescent probe technique has attracted increasing attention owing to its easy preparation, high sensitivity and selectivity, real-time detection.19-29

In recent years, a large number of excellent fluorescent probes for detecting hydrazine with good selectivity and specificity have been designed and synthesized.<sup>30-46</sup> However, many fluorescent probes suffer from complex synthesis routes, expensive raw materials and

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highly toxicity. Herein, we selected berberine as the fluorophore because of its strong fluorescence, broad source, low toxicity, and easy to be modified. Berberine (BBR), a famous natural isoquinoline alkaloid extracted from Chinese herbs Coptidis rhizoma, has been widely used as anti-influenza agent,<sup>47</sup> antibiotics,<sup>48</sup> anticancer and antioxidant,<sup>49</sup> cancer immunotherapy agents<sup>50</sup> and antiplasmodial.<sup>51</sup> In recent years, a series of berberine derivatives have been designed and synthesized.<sup>52-60</sup> However, most of researches have focused on its biology and pathophysiology ignoring their fluorescence properties. In this paper, a novel colorimetric and fluorimetric probe BP based on berberine was reported, which was responsive to hydrazine. Furthermore, the probe BP has short synthesis route, lower detection limit, convenient naked-eye detection, highly selectivity and specificity.

#### 2 Results and discussion

#### 2.1 Solvent effect on the fluorescence spectra test

In order to choose a suitable solvent in the spectrum test, fluorescence spectra of BP in different solvent was tested. As shown in Fig. 1, the different solvents strongly influenced on the



Fig. 1 Fluorescence spectra of **BP** (50  $\mu$ M) in the different kinds of solvents.

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fluorescence intensity and the peak position. **BP** in CH<sub>3</sub>CN, C<sub>2</sub>H<sub>5</sub>OH and DMSO showed strong fluorescence, whereas THF and PBS (pH = 7.4) solution showed weak/no fluorescence. However, **BP** showed stronger fluorescence and larger wavelengths in CH<sub>3</sub>CN than that in C<sub>2</sub>H<sub>5</sub>OH and DMSO. Therefore, the subsequent spectrum tests were performed in CH<sub>3</sub>CN.

#### 2.1 General UV-vis and fluorescence spectra measurements



Fig. 2 Absorption (a) and fluorescence emission (b) spectra of BP (50  $\mu$ M) in CH<sub>3</sub>CN in the absence (black) or presence (red) of N<sub>2</sub>H<sub>4</sub> (500  $\mu$ M). Each spectrum was acquired at 60 min after the addition of  $N_2H_4$ .  $\lambda_{ex}$  = 380 nm. Inset: color change of **BP** (50  $\mu$ M) solution after the addition of  $N_2H_4$  (500  $\mu$ M) under sunlight and 365 nm UV light.

The spectroscopic properties of BP (50 µM) with and without 10 equiv. of hydrazine (500 µM) were first investigated by UV-vis absorbance and fluorescence emission spectroscopy at room temperature. As shown in Fig. 2a, BP exhibited a strong absorption peak at 343 nm and a weak absorption peak at 425 nm. Upon the addition of hydrazine, the absorption peak at 343 nm and 425 nm decreased and new absorption peaks at around 377 nm and 500 nm appeared obviously with a significant red shift in the maximum absorption wavelengths (34 nm and 75 nm, respectively). The color of the solution changed clearly from green to red (Fig. 2a) and indicated that BP could be used for colorimetric detection of hydrazine by naked eye.

Meanwhile, the addition of hydrazine to the solution of BP can cause an obvious decrease of fluorescence intensity at 550 nm (Fig. 2b). At the same time, **BP** showed a distinct fluorescent color change from bright yellow-green to dark red.



Fig. 3 The time-dependent absorption spectra (a) and intensity (500 nm) (b) of **BP** (50 M) in the presence of  $N_2H_4$  (500  $\mu$ M). Inset: Color changes of **BP** (50  $\mu$ M) solution after the addition of N<sub>2</sub>H<sub>4</sub> (500  $\mu$ M) under sunlight.

#### 2.2 Kinetic studies

The reaction time of **BP** for detecting hydrazine was measured. Time dependent absorption spectra of BP were monitored in the presence of hydrazine in acetonitrile. As shown in Fig. 3, a significant change of absorption intensity was noted within 60 min with a naked-eye color change from green to red, which indicated that the reaction between BP and hydrazine was complete (Fig. 3b). Therefore, a reaction time of 60 min was selected in the next experiments.

#### 2.3 Titration studies of probe

The titration experiments of BP towards hydrazine were studied by measuring its UV-vis absorption and fluorescence spectra. As shown in Fig. 4a, with the increasing concentration of hydrazine, the intensity in absorption bands at 343 nm and 425 nm gradually quenched and new absorption peaks at around 377 nm and 500 nm enhanced obviously, and a satisfactory linear relationship between the hydrazine concentration and absorbance intensity was observed (Fig. 4b). With increasing the concentration of hydrazine, the fluorescence intensity at 550 nm was obviously quenched until disappearance (Fig. 4c).

In order to explore the detection limit of BP, the emission intensity of BP was measured for 9 times and the standard variance was 5.83. A good linear relationship between fluorescence intensity and hydrazine concentration was observed in the range of 1~7 equiv. (Fig. 4d), and the fitted linear equation is: y = -12.7317 x +595.4399. The detection limit (DL) of BP toward hyd calculated to be as low as 1.37 µM based on the general 3



Fig. 4 UV-vis absorption (a) and fluorescence spectra (  $\mu$ M) with the concentration of N<sub>2</sub>H<sub>4</sub> (0-500  $\mu$ M),  $\lambda$ ex = The linearity of the UV-vis absorption at 343 nm concentration of N<sub>2</sub>H<sub>4</sub>. Inset: the intensity of UV-vis ab 343 nm with the concentration of N<sub>2</sub>H<sub>4</sub>. (c) The linea fluorescence intensity at 550 nm with the concentration Inset: the intensity of fluorescence intensity at 550 nr concentration of N<sub>2</sub>H<sub>4</sub>.

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#### 2.4 Selectivity and specificity study

In order to evaluate the selectivity of **BP** toward hydrazine, various species including metal ions, anions and amines were tested. As shown in Fig. 4a, after addition of the analytes species, including metal ions:  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Hg^{2+}$ ,  $Na^+$ ,  $Cr^{3+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ; anions:  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $Br^-$ ,  $H_2PO_4^-$ ,  $HSO_3^-$ ; amines: phenylalanine (Phe), urea, L-asparagine (Asn), L-threonine (Thr), L-cysteine (Cys), 1,2-diaminobenzene (OPD), cyclohexane (Cyh), hydroxylamine (Hya), 2-hydrazinopyridine (Hyp); the absorption peak of **BP** and other various analytes displayed a major absorption peak at 343 nm and 425 nm. However, upon addition of hydrazine, the maximum absorption peak of **BP** red-shifted 34 nm from 343 nm to 377 nm and 75 nm from 425 nm to 500 nm, respectively (Fig. 5a). Meanwhile, only a naked-eye color change from green to red was noticed upon addition of hydrazine (Fig. 5b).

Among the various ions added, the other ions showed no obvious fluorescence decrease and color change, only hydrazine promoted a significant fluorescence 'on-off' response at 550 nm in fluorescence intensity. The results exhibited that **BP** possesses high selectivity toward metal ions (Fig. 6a), anions (Fig. 6b) and amines (Fig. 6c). However, when some analytes were added, the fluorescence



Fig. 6 Fluorescence spectra of probe BP (50  $\mu M)$  upon addition of  $N_2H_4$  (500  $\mu M)$  and various analytes (500  $\mu M).$ 



Fig. 7 Fluorescence responses of **BP** (50  $\mu$ M) upon addition of different species (500  $\mu$ M) individually and fluorescence changes of the mixture of **BP** and N<sub>2</sub>H<sub>4</sub> (500  $\mu$ M) after addition of an excess of the competitive analytes (500  $\mu$ M) with emission intensity at 550 nm. The reaction time was 60 min. (competitive analytes : metal ions: 1: Zn<sup>2+</sup>, 2: Co<sup>2+</sup>, 3: Hg<sup>2+</sup>, 4: Na<sup>+</sup>, 5: Cr<sup>3+</sup>, 6: Ca<sup>2+</sup>, 7: Cu<sup>2+</sup>, 8: Fe<sup>3+</sup>; anions: 1: Cl<sup>-</sup>, 2: NO<sub>3</sub><sup>-</sup>, 3: SO<sub>4</sub><sup>2-</sup>, 4: CO<sub>3</sub><sup>2-</sup>, 5: Br<sup>-</sup>, 6: H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, 7: HSO<sub>3</sub><sup>-</sup>; amines: 1: Phe, 2: Urea, 3: Asn, 4: Thr, 5: Cys, 6: OPD, 7: Cyh, 8: Hya, 9:Hyp.

intensity of **BP** showed a degree of increase or decrease, which may be caused by the solubility and activity of berberine compounds. As showed in Fig. 7, the interference test showed that other competitive analytes could hardly influence on the detection of hydrazine in a complex environment. The result confirmed that **BP** is a specific fluorescent probe for detection towards hydrazine.

#### 2.5 Sensing mechanism

As shown in **Scheme 1**, firstly, hydrazine can selectively attack the carbonyl group on aromatic ester of **BP** and then leading to cleavage of the ester group to obtain an important intermediate compound.<sup>61</sup> Meanwhile, the green fluorescence of **BP** was disappeared. Secondly,



Scheme 1 The proposed reaction mechanism of **BP** for sensing hydrazine.

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Fig. 8 Liquid chromatogram analysis (a) and mass spectrum analysis (b) of **BP**, **BP**+N<sub>2</sub>H<sub>4</sub> and berberrubine; UV–vis absorption (c) and fluorescence intensity (d) of **BP** (50  $\mu$ M), BP (50  $\mu$ M) + N<sub>2</sub>H<sub>4</sub> (500  $\mu$ M) and berberrubine (600  $\mu$ M). Inset: color changes of **BP**, **BP**+N<sub>2</sub>H<sub>4</sub> and berberrubine under sunlight and a 365 nm UV lamp.

the intermediate undergo electron transfer process and aromatic hydrazine is eliminated to afford zwitterionic form 2a, which resulted in the fluorescence quenching via photoinduced electron transfer (PET). Then quinoid structure 2 (berberrubine) which structure was confirmed by NMR spectrum was obtained as result of tautomerization process.<sup>62</sup>

In order to further confirm and understand the sensing mechanism, LC-MS analysis was performed (Fig. 8), we measured the LC-MS spectra of the sensing reaction compared with berberrubine and **BP**. As show in Fig. 8a, retention time of probe **BP** in liquid chromatography was 1.784 min after the addition of hydrazine, and berberrubine was 1.762 min. The molar mass of **BP** after addition of N<sub>2</sub>H<sub>4</sub> agreed well with berberrubine (m/z = 322.1 for **BP**+ N<sub>2</sub>H<sub>4</sub>; m/z = 322.2 for berberrubine) (Fig. 8b). Moreover, the UV-vis absorbance (Fig. 8c) and fluorescence intensity (Fig. 8d) of **BP** after addition of N<sub>2</sub>H<sub>4</sub> also agreed well with berberrubine. The above results demonstrated that the detection of hydrazine for **BP** is indeed basing on the proposed mechanism shown in Scheme 1.

#### 2.6 Theoretical calculation

To further understand the changes and optical responses of **BP** to hydrazine, a theoretical calculation was carried out by Density Functional Theory (DFT). The optimized configurations and corresponding the LUMO (the lowest unoccupied molecular orbitals) and HOMO (the highest occupied molecular orbitals) were performed.<sup>63,64</sup> As shown in Fig. 9, **BP** has  $\pi$ - $\pi$  conjugate effect and emits strong fluorescence intensity due to the effect of the internal charge transfer (ICT). However, after the nucleophilic addition of hydrazine to the carbonyl group, the compound **2a** changed to compound **2** via photo-induced electron transfer (PET) (Scheme 1). Meanwhile, the fluorescence of compound **2** was disappeared. Therefore, the energy gaps between the HOMO and LUMO of were



Fig. 9 Optimized structures and HOMO/LUMO of **BP** and compound **2** by DFT calculation.

calculated to 3.75 and 2.96 eV for **BP** and compound **2**, respectively. And the energy gap also ascribed the red shift of the UV–vis spectra.

#### 2.7 Detection of gaseous hydrazine

To explore the practical applications of **BP**, it was also utilized for the detection of hydrazine gas. For this test, glass TLC plates were soaked in a CH<sub>3</sub>CN solution of **BP** (1.0 mM) and dried. Then, the TLC plates were placed in airtight bottles containing different concentrations of hydrazine (1%, 10%, 20%, 40% and 80%) for 60 min at room temperature. As showed in Fig. 10, the colors of the glass TLC plates change from green to tan and the fluorescent color turn from yellow-green into colorless with the increasing hydrazine concentration (from 1% to 80%). The results indicated that the **BP**coated TLC plates exhibited high sensitivity for hydrazine vapor and the hydrazine gas in the different hydrazine solutions can be expediently monitored by naked-eyes and UV lamp (excitation wavelength 365 nm).



Fig. 10 Photographs for **BP** (1.0 mM) coated TLC plates upon exposure to different hydrazine solutions vapored from different concentrations of hydrazine aqueous solution (1%, 10%, 20%, 40%, 80%, w/w) for 60 min. Upper: under ambient light; Lower: under a UV lamp with an excitation at 365 nm.

#### 3 Experimental

#### 3.1 Methods and materials

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All chemicals and solvents were purchased from commercial sources and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR were measured on a Bruker 400 MHz spectrometer. UV-Vis absorption spectra were recorded by a Shimadzu UV-2450. Fluorescence emission spectra were tested using PerkinElmer LS55. Highresolution mass spectra (HR-MS) were tested by an America Agilent 5975c mass spectrometer.

#### 3.2 General procedures for analysis

In this test, the solution of probe **BP** was prepared to be 50  $\mu$ M with acetonitrile and the hydrazine solution (500  $\mu$ M) was dissolved in distilled water. Meanwhile, the stock solutions of relevant analytes (0.01 M) were manufactured in distilled water, including metal ions (Zn<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Na<sup>+</sup>, Cr<sup>3+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>), anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, Br<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HSO<sub>3</sub><sup>-</sup>), and amines (phenylalanine (Phe), urea, L-asparagine (Asn), L-threonine (Thr), L-cysteine (Cys), 1,2-diaminobenzene (OPD), cyclohexane (Cyh), hydroxylamine (Hya), 2-hydrazinopyridine (Hyp). The excitation wavelength was set at 380 nm. The incident slit width was 5.0 nm and exit slit was 7.0 nm.

#### 3.3 Synthesis of probe BP



# Scheme 2 Synthesis of BP

### 3.3.1 Synthesis of compound 2

Berberine chloride (10.0 g, 26.9 mmol) was heated at 180–190°C for 30–60 min under vacuum to afford dark wine solid, which was washed with MeOH (80 mL) and filtered to afford compound **2** (Berberrubine) (6.7 g, 76.7%). <sup>1</sup>H NMR (400 MHz, Methanol- $d_4$ )  $\delta$  (ppm): 9.24 (s, 1H), 7.96 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.40 (s, 1H), 6.85 (d, J = 9.0 Hz, 2H), 6.05 (s, 2H), 4.60 (t, J = 6.0 Hz, 2H), 3.88 (s, 3H), 3.13 (t, J = 6.0 Hz, 2H); 13C NMR (400 MHz, Methanol- $d_4$ )  $\delta$  (ppm): 164.35, 151.06, 150.82, 149.43, 147.26, 135.47, 133.65, 130.63, 124.08, 122.85, 121.63, 119.62, 109.20, 108.26, 105.79, 103.25, 56.75, 55.54, 28.94; ESI-MS (m/z): calcd. for [M+H]<sup>+</sup> : 322.1079, found : 322.1095.

### 3.3.2 Synthesis of probe BP

The solution of compound **2** (2.0 g, 6.23 mmol) in CH<sub>3</sub>CN (30 mL) benzoyl chloride (1.0 g, 7.48 mmol) were added slowly under an nitrogen atmosphere. Reaction mixture was allowed to stir for 3 h at 80 °C. Solvent was evaporated under vacuum and crude product was washed with dichloromethane/diethyl ether to afford **BP** (1.7 g, 76.7 %). 1H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.00 (s, 1H), 9.13 (s, 1H), 8.29 (dd, J = 16.0, 9.6 Hz, 4H), 7.83 (m, 2H), 7.70 (t, J

= 7.6 Hz, 2H), 7.07 (s, 1H), 6.17 (s, 2H), 4.92 (t,  $J = 0.6 \text{ M}^2$ , 2H), 4.02 (s, 3H), 3.20 (t, J = 6.4 Hz, 2H). 13C NMR (400<sup>3</sup> MP2, DMSO)  $d_6$ )  $\delta$  (ppm): 163.38, 150.39, 149.95, 147.67, 144.44, 138.10, 134.54, 133.56, 132.98, 130.81, 130.38, 129.05, 127.96, 126.95, 125.86, 121.19, 120.65, 120.30, 108.36, 105.55, 102.10, 57.29, 55.22, 26.14. ESI-MS (*m*/*z*): calcd. for [M-CI]<sup>+</sup>: 426.1336, found: 426.1339.

# 4 Conclusions

In summary, we have described a novel berberine-based naked-eye and fluorescence probe for hydrazine detection. The probe **BP** showed high selectivity and specificity toward hydrazine over other various analytes. Meanwhile, a color changes from green to red for detection by the naked-eye, which can easily and rapidly detect hydrazine. Moreover, this probe exhibited short synthesis route (2 steps), lower detection limit (1.37  $\mu$ M) and excellent fluorescence properties. The sensing mechanism of **BP** was confirmed by LC-MS analysis, optical test and DFT calculation. In addition, **BP** was also successfully used to detect hydrazine gas at different concentrations.

# **Conflicts of interest**

The authors declare no competing interests.

## Acknowledgements

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# A novel berberine-based colorimetric and fluorimetric probe for

# hydrazine detection

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Hydrazine in water and soil has caused a serious disease threatening human health. It is critical to develop a simple and effective method for detecting hydrazine. In this work, a simple fluorescent probe (**BP**) was synthesized for hydrazine detection based on berberine. The probe has short synthesis route (2 steps), low detection limit (0.29  $\mu$ M), excellent fluorescence properties and convenient naked-eye detection. In addition, **BP** displayed excellent selectivity and specificity over other metal ions, anions and amines. Moreover, **BP** was also successfully used to detect hydrazine gas at different concentrations.

