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4-(8-Quinolyl)amino-7-nitro-2,1,3-benzoxadiazole as a new selective and sensitive fluorescent and colorimetric pH probe with dual-responsive ranges in aqueous solutions

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ABSTRACT

Fluorescent and colorimetric pH probe possess many advantages including rapid response time, nondestructive testing, and excellent pH sensitivity. However, they usually cannot be utilized simultaneously in both acidic and basic pH ranges. In this study, a new selective and sensitive fluorescent and colorimetric pH probe, 4-(8-quinolyl)amino-7-nitro-2,1,3-benzoxadiazole (**1**), was designated and synthesized. The optical probe exhibited dual-responsive pH ranges to both acidic and basic aqueous solutions. When the solution pH was gradually increased from 8.5 to 13.3, the absorption spectra of **1** showed an obvious hyperchromicity, accompanied with a red shift of the absorption band at 340 nm, a blue shift of the absorption band at 482 nm, and a distinct color change from orange to violet pink to yellow. Within the pH range from 2.2 to 0.2, the fluorescent spectra of **1** showed a "turn-on" response signal to solution pH. In order to understand the response mechanism of the probe to solution pH, the probe molecule was split into two parts, 8-aminoquinoline (**2**) and 4-amino-7- nitro-benzofurazan (**3**). UV–vis absorption and fluorescent experiments of **2** and **3** indicated that both are sensitive optical pH probes. Furthermore, the NMR experiment of **1** was explored in basic and acidic conditions. The results indicated that the colorimetric responses of **1** to pH under basic condition should be attributed to the deprotonation of the imino group on the quinolyl ring, and the fluorescent recognition of **1** to pH under acidic condition was probably due to the protonation of the nitrogen atoms from the benzofurazan and quinolyl rings.

1. Introduction

The pH value plays a pivotal role in chemical reactions and biological processes [1–4]. It not only has significant effects for the physical and chemical properties and reactivity of substances but it also has an important function on the life system [5,6]. Many available methods have been reported to measure pH values, such as acid–base indicator titration [7–10], microelectrodes [11], nuclear magnetic resonance (NMR) [12], potentiometric titration [13–15], absorption and fluorescent spectroscopy[16–19]. Among these methods, fluorescent and colorimetric probe is a powerful tool for the handy, rapid, low-cost, highly selective and sensitive, and nondestructive measurement of pH value, especially to clarify the real-time dynamics and various biological processes in living cells. In recent years, a large variety of fluorescent and colorimetric pH probes were fabricated successfully [18–22]. Unfortunately, most of the reported optical probes could only be used in a single pH range, and they could not be utilized in both acidic and basic pH ranges [23]. In this work, we developed a new optical pH probe 4-(8-quinolyl)amino-7-nitro-2,1,3-benzoxadiazole (**1**) which can monitor pH ranges from 2.2 to 0.2 with a p*K*a value 1.4 and from 8.5 to 13.3 with a p*K*a value 10.5. The experiment results indicated that **1** was a sensitive fluorescent and colorimetric pH probe with dual-responsive ranges, and could be used under both acidic solution and basic solution. In addition, two components of probe **1**, 8-aminoquinoline (**2**) and 4-amino-7-nitro-benzofurazan (**3**), were also sensitive optical pH probes.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from commercial sources and used without further purification.

Mass spectra were carried out on a LCQDACAXPMAX mass spectrometer (Finnigan). ^{1}H NMR spectra were recorded on a Varian NMR Systems 400 MHz spectrometer using TMS as the internal standard. All fluorescent emission spectra were recorded with a Hitachi F-2500

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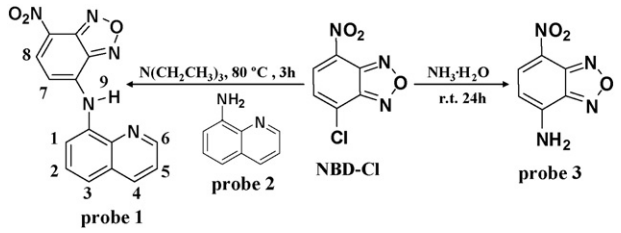

Scheme 1. Synthetic routes for probes **1** and **3**.

fluorescence spectrophotometer. UV–vis absorption spectra were determined on a Shimadzu UV-1700 spectrophotometer at room temperature. All the pH values of aqueous solutions were measured precisely with a PHS-3B digital pH meter.

2.2. Synthesis and characterization of probe 1

Sensor **1** was synthesized through a one-step reaction using 4-chloro-7-nitrobenzofurazan (NBD-Cl) and 8-aminoquinoline (**2**) (refer to Scheme 1). **2** (0.053 g, 0.37 mmol) was dispersed in 10.0 mL NEt_3. Then NBD-Cl (0.073 g, 0.37 mmol) dispersed in 5.0 mL NEt_3 was added to the above solution dropwise, and the resulting mixture was stirred for 30 min at room temperature, followed by a reflux under 80 °C for 3 h [24]. After removing the solvent, the resulting **1** was further purified using column chromatography on silica gel (elution with dichloromethane), with purified 1 in 63.5% yield. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, ppm): 11.01(s, 1H), 8.93(d, 1H), 8.51(m, 2H), 7.96(m, 2H), 7.69(m, 3H), 6.72(d, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 103.72, 121.61, 122.59, 123.84, 125.91, 126.83, 128.74, 134.30, 136.82, 137.52, 140.90, 141.71, 143.92, 145.21, and 150.20. ESI-MS (m/z): 306.24; calcd for $[1-H]^-$, 306.26.

2.3. Synthesis and characterization of probe 3

Under nitrogen atmosphere, the mixture of NBD-Cl (0.203 g, 1.0 mmol), ammonium hydroxide (4.0 ml, 30 wt.%), and methanol (20.0 mL) was stirred at room temperature for 24 h. Then, the solvent was removed, and the resulting crude product of **3** (see Scheme 1) was further purified using column chromatography on silica gel (elution with n-hexane: ethyl acetate = 1:1), achieving purified **3** in 60.03% yield. ^{1}H NMR (400 MHz, CD_3OD, 298 K, ppm): 8.49(d, 1H),6.39(d, 1H). ESI-MS (m/z): 180.12; calcd for $[\mathbf{3}+H]^+$, 180.11.

2.4. Measurements of UV–vis absorption and fluorescent spectra

All UV–vis absorption and fluorescent experiments were carried out in a buffer-DMSO (98:2, v/v) solution at 25 °C. And the buffered solutions with various pH values were modulated by mixing 3.0 mM homologous sodium salt: acetate (NaAc–HAc, pH = 3.6–5.8), phosphate (Na_2HPO_4–NaH_2PO_4, pH = 5.8-8.0), borate ($Na_2B_4O_7$–H_2BO_3, pH = 8.0–9.0) and carbonate (Na_2CO_3–$NaHCO_3$, pH = 9.0–10.8), respectively. Other pH values of the solution were adjusted by adding small amounts of 1.0 M NaOH solution or 1.0 M HCl solution. Prior to UV–vis absorption and fluorescent measurement, solutions were kept at room temperature for 24 h. A fixed excitation wavelength at 450 nm was used as the emission spectra. The concentrations of **1**, **2** and **3** in all the fluorescent and UV–vis experiments are 2.0×10^{-5} mol L^{-1} in buffered solutions.

3. Results and discussion

3.1. UV–vis response of 1 to pH changes

As shown in Fig. 1, when pH value is 8.5, the absorption spectra of **1** exhibited two weak absorption bands at 340 nm and 482 nm in aqueous solution. As the pH value of **1** solutions increased from 8.5 to 13.3, the absorption spectra of **1** showed an obvious hyperchromicity, accompanied with a red shift of the absorption band at 340 nm, and a blue shift of the absorption band at 482 nm. When the pH value rose to 13.3, the intensity of absorption bands of **1** showed no further change. Meanwhile, the position of two absorption bands shifted from 340 nm and 482 nm to 390 nm and 450 nm, and color changed from orange to violet pink to yellow (see inset in Fig. 1A). Especially, the absorption spectra could be recovered when the pH was re-adjusted back from 13.3 to 8.5. The absorption bands at 340 nm and 482 nm were mainly attributed to the characteristic absorption bands of 2,1,3-benzoxadiazole [24,25]. Thus, the remarkable changes of UV–vis absorption spectra should be attributed to the deprotonation of the imino group on 2,1,3-benzoxadiazole of **1**, which can cause a significant influence on the charge density of the benzoxadiazole aromatic nucleus. Consequently, changing of the charge–transfer interactions between electron-rich and electron-deficient moieties resulted in a clear absorption band shift [26].

Meanwhile, the variational ratios of absorption intensity at 450 nm, $(A-A_0)/A_0$, for **1** with varying pH were showed in Fig. 1B, with a 26.7-fold gain at pH 13.3 when compared with that observed at pH 8.5. The result showed a "turn-on" response in UV–vis absorption spectra for **1** to pH in basic aqueous solution. The p*K*a value of probe **1** was calculated by Henderson–Hasselbach-type equation [27,28], which gave a p*K*a value of 10.5.

When the pH value gradually changed from alkaline to weakly acidic, only a slight undulation of UV–vis absorption spectra were induced. However, when pH value was less than 3.0, obvious changes in the absorption spectra of **1** were observed, as shown in Fig. 2A. The absorption bands at 338 nm and 476 nm showed a hypochromicity with the gradual decrease of pH value from 3.1 to

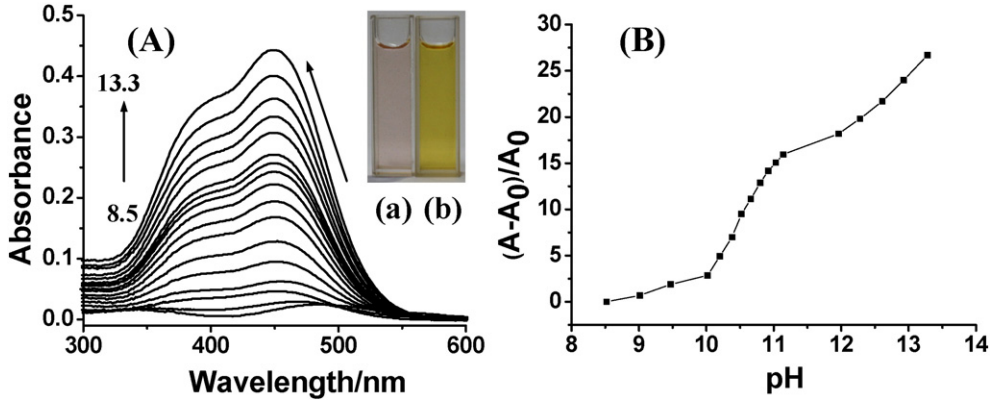

Fig. 1. (A) Absorption spectra of **1** (pH 8.5–13.3), inset: photographs of probe **1** at pH value are (a) 8.5 and (b) 13.3. (B) The change amount of absorption band intensity of **1** at 450 nm, $(A-A_0)/A_0$, as a function of pH values.