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PII: S1386-1425(15)30219-5
DOI: doi: 10.1016/j.saa.2015.09.006
Reference: SAA 14070

To appear in:

Received date: 16 April 2015
Revised date: 4 September 2015
Accepted date: 11 September 2015

Please cite this article as: Xutian Li, Min Zhang, Haipeng Liang, Zhaowei Huang, Jiang Tang, Zhi Chen, Liting Yang, Li-Jun Ma, Yuhai Wang, Baiping Xu, 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, (2015), doi: 10.1016/j.saa.2015.09.006

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 possesses many advantages including rapid response time, nondestructive testing, and excellent pH sensitivity. However, they usually can not 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 solution. 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.

Keywords

Fluorescent pH probe, Colorimetric pH probe, Aminoquinoline, 2,1,3-Benzoxadiazole, Dual-responsive range

Introduction

The pH value plays a pivotal role in chemical reactions and biological processes [1-4]. It not only for the physical and chemical properties and reactivity of substances has significant effect but also has an important function on the life system [5, 6]. Many available methods have been reported to measure pH value, 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], etc. 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.

Experimental

Materials and methods

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

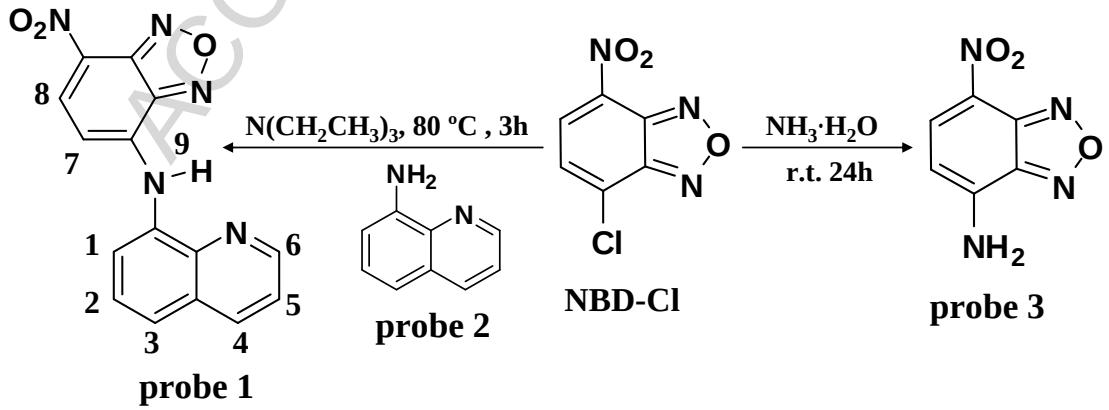
Mass spectra were carried out on a LCQDACAXPMAX mass spectrometer (Finnigan). ^{1}H NMR spectra were recorded on a Varian NMR Systems 400 MHz spectrometer using TMS as the internal standard. All fluorescent emission spectra were recorded with a Hitachi F-2500 fluorescence spectrophotometer. UV-vis absorption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

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 reflux under 80 °C for 3 h [24]. After removing the solvent, the resulting **1** was further purified using column chromatography on silicagel (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, 150.20. ESI-MS (m/z): 306.24; calcd for $[1\text{-H}]^-$, 306.26.

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 silicagel (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 $[\mathbf{3}+\text{H}]^+$, 180.11.



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

Measurements of UV-vis absorption and fluorescent spectra

All UV-vis absorption and fluorescent experiments were carried out in 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 value of the solution was 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 concentration of **1**, **2** and **3** in all the fluorescent and UV-vis experiments is 2.0×10^{-5} mol L^{-1} in buffered solutions.

Results and discussion

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].

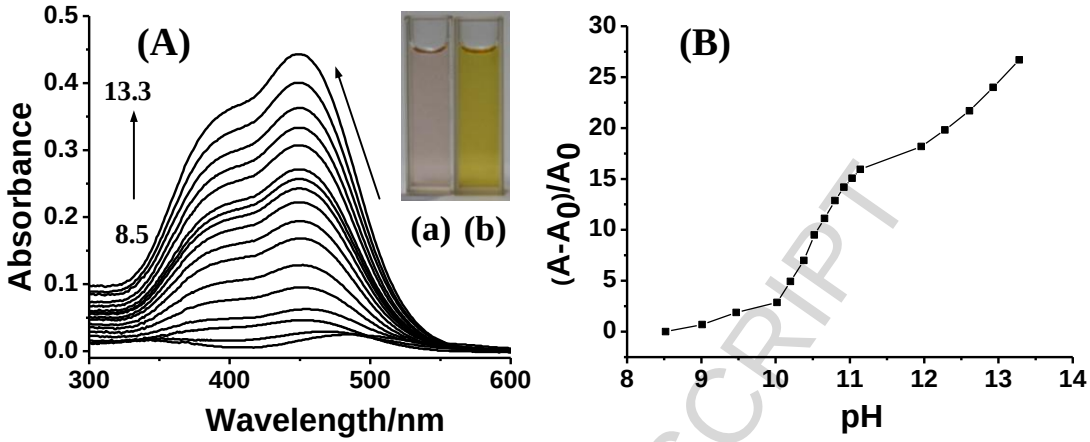


Fig. 1. (A) Absorption spectra of **1** (pH 8.5-13.3), Inset: photographs of probe **1** at pH value is (a) 8.5 and (b) 13.3. (B) The change amount of absorption band intensity of **1** at 450 nm, $(A-A_0)/A_0$, as a function of pH values.

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 to 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 slight undulation of UV-vis absorption spectra was 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 1.3. Then, when pH value decreased from 1.3 to 0.2, the spectra showed the red shifts of the absorption bands from 338/476 nm to 315/457 nm with an obvious hyperchromicity. When the pH was re-adjusted from 0.2 to 3.1, the absorption spectra could be recovered. The experiment phenomenon probably induced by the protonation of the nitrogen atoms on the benzofurazan and quinolyl ring of **1** at strong acid condition, which caused a decrease of the charge density of the aromatic nucleus in **1**.[26]

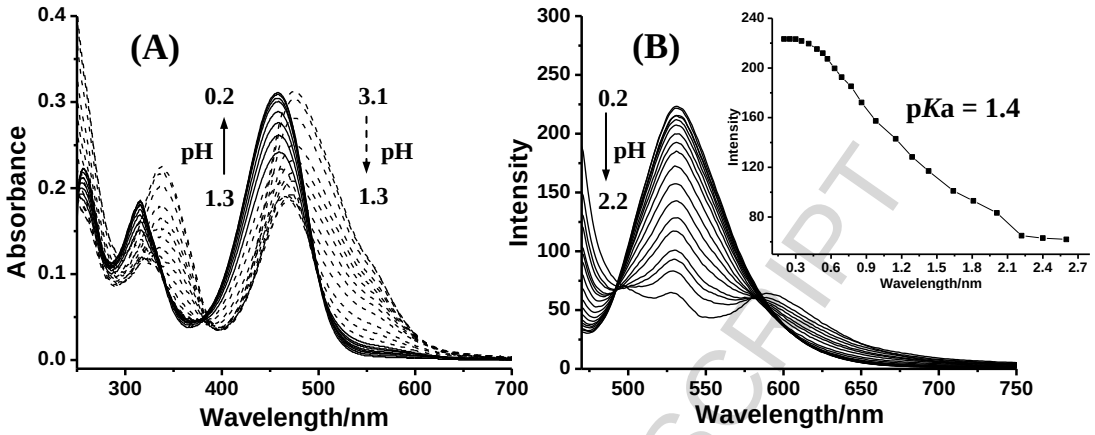


Fig. 2. (A) Absorption spectra of **1** (pH 3.1-0.2). (B) Fluorescent spectra of **1** at various pH values (pH 2.2-0.2, λ_{em}=450 nm); Inset: the variation of fluorescent emission intensity of **1** at 531 nm with pH (pH 2.6-0.2).

Fluorescent response of 1 to strong acid

The fluorescent spectra of **1** were measured under the various pH values. The experiment results under alkaline and weak acidic conditions indicated that the probe **1** only shows very weak fluorescent emission, which was potentially due to blockage of intramolecular charge transfer (ICT) process for benzofurazan ring with two electron-deficient group (nitro group and quinoline ring) [29]. However, as shown in Fig. 2B, with the gradual decrease of pH value from 2.2 to 0.2, obvious enhancement of the fluorescent emission of **1** was observed, resulting in a 2.5-fold gain at 531 nm at pH 0.2 when compared to that observed at pH 2.2. Meanwhile, the fluorescent band of **1** at 590 nm was quenched. The fluorescent band at 590 nm was assigned to a characteristic emission of benzofurazan group, which may overlap the characteristic emission of the quinoline group whose fluorescent emission was very weak. Moreover, the fluorescent enhancing could be recovered when the pH was re-adjusted from 0.2 to 2.2. The result indicated that **1** was a sensitive fluorescent switch to pH/H^+ within the pH range from 2.2 to 0.2. The fluorescent enhancement response was consistent with the results from the UV-vis absorption spectra, where the protonation of the nitrogen atoms in the benzofurazan and quinolyl rings of **1** was bring the ICT between electron-rich and electron-deficient moieties on benzofurazan group. Thus, the fluorescent emission was increased at strong acid condition. In addition, the analysis of fluorescent intensity changes of **1** as a function of pH by the Henderson–Hasselbach-type mass action equation [28] yielded a p*K*a of 1.4 for **1** (298 K), which indicated its usefulness for the investigation in strong acidic condition (see

inset of Fig. 2B).

Interference experiment

To test the practical application of **1** in the fluorescent detection for pH, interference experiments were performed to estimate the influence caused by other ions which may be present in the systems being analyzed. The relative fluorescent intensities of **1** in the absence or presence of an excess of Cr^{3+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Mn^{2+}, Na^{+}, Zn^{2+}, Ni^{2+} and Hg^{2+} (100.0 μM) at pH 0.7 were shown in Fig. 3. The results indicated that the effect of these metals on pH measurement should be negligible. Therefore, **1** can be used as a potential probe for the practical detection of pH changes in strong acidic aqueous solution.

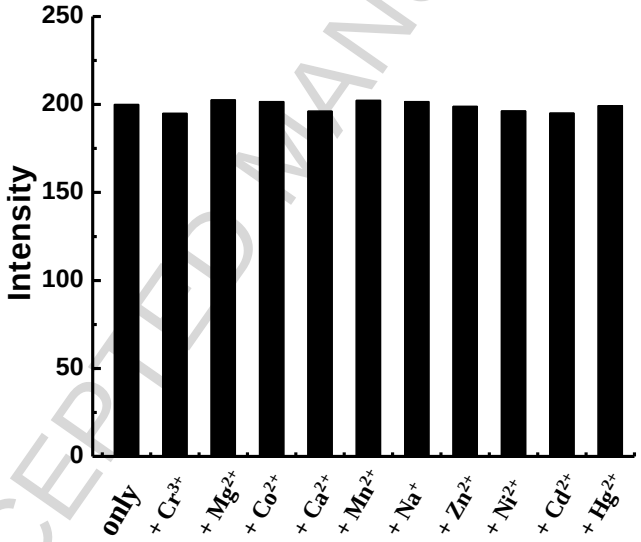


Fig. 3. Fluorescent intensity at 531 nm of **1** in the absence or presence of Cr^{3+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Mn^{2+}, Na^{+}, Zn^{2+}, Ni^{2+} and Hg^{2+} (100.0 μM), respectively, at pH 0.7.

The response mechanism of 1 to pH changes

In order to understand the response mechanism of the probe to pH value, the probe molecule was split into two parts, 8-aminoquinoline (**2**) and 4-amino-7-nitro-benzofurazan (**3**), and their UV absorption and fluorescent spectra under the various pH values were examined.

UV-vis response of 2 to pH changes

As shown in Fig. 4A, the UV-vis absorption spectra of **2** showed an absorption band at 332 nm in neutral or alkaline condition. However, with gradual decrease of pH value of the solution from 6.0 to 1.0, the absorption band at 332 nm was weakened gradually, while a new absorption band at 386 nm increased gradually, and the color

of the solutions of **2** changed from the original colorless to yellow (see inset of Fig. 4A). The results were due to the protonation of imino group and nitrogen atom on the quinoline ring of **2**, which changed the charge density on the aromatic nucleus of **2** and resulted in the red shift of absorption band. The fluorescent spectra of **2** also were tested under different pH values conditions, and the results showed that the probe **2** scarcely shows fluorescent emission. These results showed that **2** is a colorimetric pH probe in acidic condition. The p*K*a value of probe **2** has been calculated by Henderson-Hasselbach-type equation [27, 28], which gave a p*K*a value of 3.9 [30]. Compared to the above UV-vis and fluorescent data of probe **1**, these results indicated that the colorimetric response under alkaline condition and the fluorescent recognition of **1** to pH under acidic condition were contributed by the benzofurazan moiety rather than the 8-aminoquinoline moiety. Meanwhile, the ratios of absorption intensity at 386 nm and 332 nm, A_{386}/A_{332}, for **2** with pH were showed in Fig. 4B. The result showed a ratiometric response in UV–vis absorption spectra for **2** to pH in acid aqueous solution.

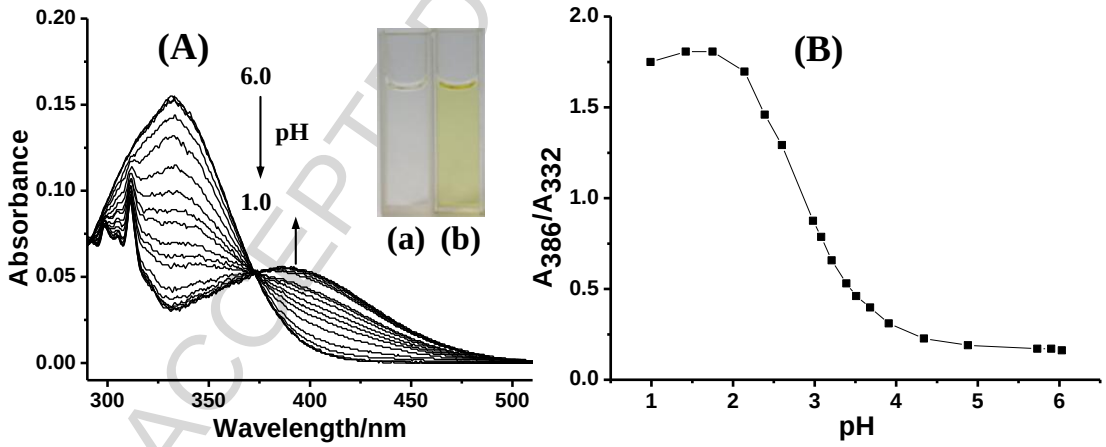


Fig. 4. (A) UV-vis absorption spectra of **2** (pH 6.0-1.0), Inset: Photographs of probe **2** in the condition of pH value is (a) 6.0 and (b) 1.0. (B) The ratio of absorption peak intensity of **2** at 386 nm and 332 nm in different pH values.

Optical response of 3 to pH changes

When the pH of the solution is 6.1, the UV-vis absorption spectra of **3** had two characteristic absorption band of benzofurazan ring at 340 nm and 467 nm, as shown in Fig. 5A. With the increase of the pH values from 6.1 to 12.3, the absorption band at 467 nm decreased gradually, and a new absorption band at 382 nm increased gradually. Meanwhile, a clear isosbestic point at 434 nm in the absorption spectra was observed, which suggested the formation of a new complex. Under the same

experimental condition, the fluorescent response of **3** to pH changes was explored. As show in Fig. 5B, the fluorescent spectra of **3** have a strong fluorescent emission peak at 543 nm. With increasing of the solution pH, the fluorescent emission intensity was gradually reduced, resulting in a 92.1% quenching from a pH of 6.1 to a pH of 12.5. Under the irradiation of 365 nm UV light, the fluorescent color of the solution turned from bright yellow to colorless. The results should be attributed to the deprotonation of amino group in probe **3**, which weakened the charge–transfer interactions between electron-rich (amino group) and electron-deficient (nitro group) moieties, inducing the clear absorption band shift and the fluorescent quenching. The UV-vis and fluorescent spectra of **3** was also explored in strong acidic condition from 3.1 to 0.2. UV-vis spectra of **3** did not show obvious changes, and its fluorescent spectra only showed weak quenching. The result showed that **3** is a fluorescent probe for pH under basic condition. Combining with the above experiment results, the UV-vis response of **1** to pH may be attributed to the deprotonation of imino group of **1** in basic condition, and fluorescent recognition of **1** to pH was contributed by the cooperative interaction between the quinoline and benzofurazan rings**.**

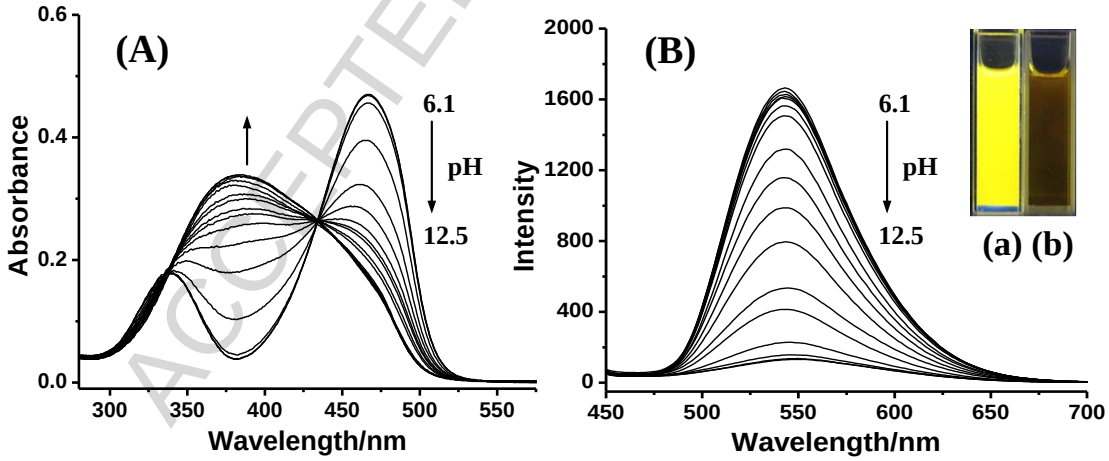


Fig. 5. (A) UV-absorption and (B) fluorescent spectra of **3** (pH 6.1-12.5, λ_{em} = 380 nm). Inset (B): fluorescent photographs of probe **3** at pH value of (a) 6.1 and (b) 12.5 under illumination with 365 nm light.

^{1}H NMR experiments of 1 in acidic and alkaline condition

To further explore the mechanism of **1** for determining the pH value, ^{1}H NMR experiments of **1** in acidic and alkaline conditions were tested in the solutions of DMSO-d_6: D_2O (10:1, v/v). As shown in Fig. 6A, with the addition of NaOH, the chemical shift of several protons on **1** was significant changed. The disappearance of

H(9) and the remarkable upfield shifts of H(1) ($\Delta\delta_{H1}$ = -1.25 ppm) and H(7) ($\Delta\delta_{H7}$ = -1.39 ppm) implied deprotonation of the imino group in probe **1**, in consistent with the UV-vis absorption spectra of **1** to pH in Fig. 1A. Moreover, after the addition of HCl, the chemical shifts for all hydrogen protons of probe **1** showed obvious changes in chemical shift, as shown in Fig. 6B. With the continuous addition of HCl, the chemical shifts of H(6), H(5) and H(4) in probe **1** showed the large changes ($\Delta\delta_{H6}$ = 0.15 ppm, $\Delta\delta_{H5}$ = 0.09 ppm and $\Delta\delta_{H4}$ = 0.09 ppm), which revealed the protonation of nitrogen atom on the quinolyl ring. Meanwhile, the obvious upfield shifts of H(7) ($\Delta\delta_{H7}$ = -0.12 ppm) and H(8) ($\Delta\delta_{H8}$ = -0.04 ppm) were observed, which indicated the increase for electron density of benzofurazan ring. The results should cause by the protonation of three nitrogen atoms on the quinoline and benzofurazan rings under acidic conditions, where the attracting for the electron of the benzofurazan ring with two protonated nitrogen atoms was stronger than the quinoline ring with one protonated nitrogen atom. ICT between electron-rich (imino group) and electron-deficient (nitro group) moieties on benzofurazan group and the fluorescent enhancing signal were generated. Thus, the colorimetric and fluorescent responses of **1** to pH should attribute to the deprotonation of the imino group of **1** and the protonation of three nitrogen atoms on the benzofurazan and quinoline rings. Based on these results, a potential response model of **1** to pH was proposed in Scheme 2.

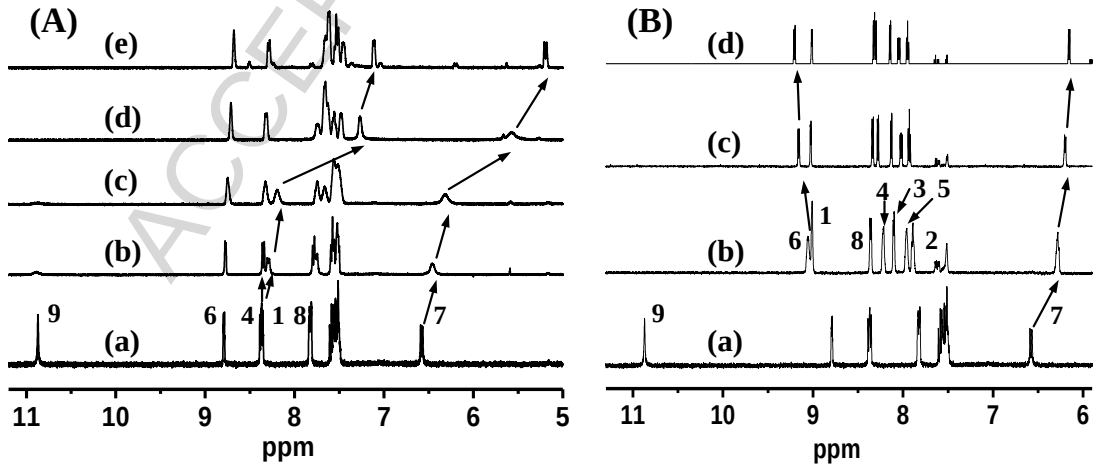
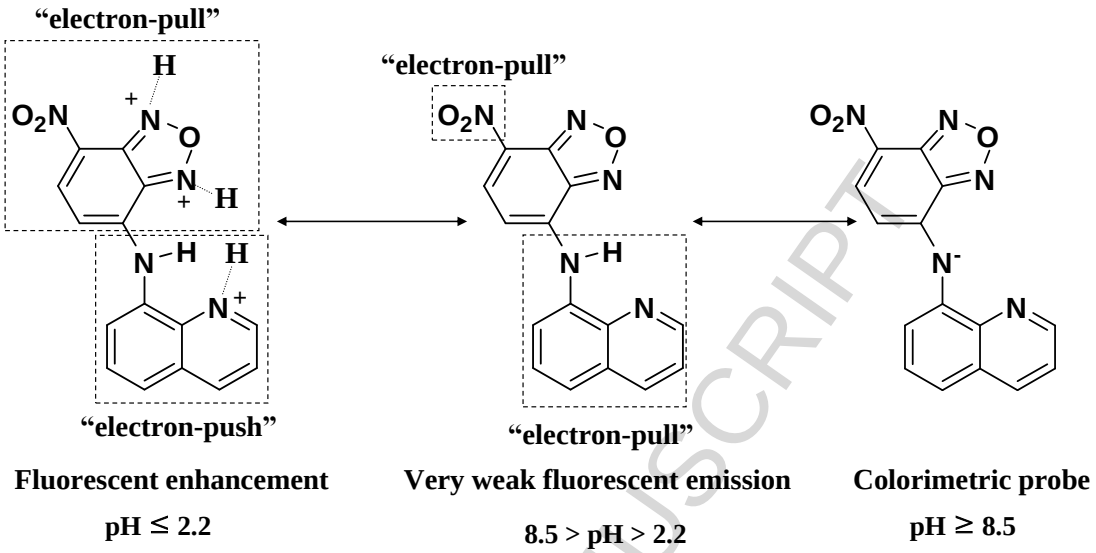


Fig. **6.** (A) ^{1}H NMR spectra of (a) **1** (10.0 mM), (b) **1**–NaOH(10:1, mol/mol), (c) **1**–NaOH (5:1, mol/mol), (d) **1**–NaOH (2:1, mol/mol), (e) **1**–NaOH (1:1, mol/mol); (B) ^{1}H NMR spectra of (a) **1**, (b) **1**–HCl (10:1, mol/mol), (c) **1**–HCl (5:1, mol/mol), (d) **1**–HCl (2:1, mol/mol) in DMSO-d_6 : D_2O (10:1, v/v).



Scheme 2. Proposed response model of **1** to pH.

Conclusions

In this study, an optical pH probe **1** with dual-responsive ranges in acidic and alkaline condition was synthesized. Under alkaline condition, **1** with a p*K*a value 10.5 could be applied as a colorimetric probe to pH change. And **1** with a p*K*a value 1.4 could be used as a fluorescent "turn-on" probe under acidic condition. The investigation for the recognition mechanism of **1** to pH variation indicated that the colorimetric responses of **1** to pH was attributed to the deprotonation of imino group of **1**, and the fluorescent recognition of **1** to pH was potentially due to the protonation of three nitrogen atoms on the benzofurazan and quinoline rings. The present work was not only a supplement to the detection method of pH value, but also a development for new optical pH probes with the dual-responsive ranges.

Acknowledgments

The authors are grateful to the project of Science & Technology New Star of Zhu Jiang in Guangzhou city (No. 2012J2200026), Guangdong Natural Science Foundation, China (Development and recognition property of new fluorescence probes for heavy metal ions, 2015), and Guangdong Province Higher Vocational Colleges & Schools Pearl River Scholar Funded Scheme (2012).

References

[1] G.K. Vegesna, J. Janjanam, J. Bi, F.T. Luo, J.T. Zhang, C. Olds, A. Tiwariand, H.Y. Liu, J. Mater. Chem. B 2 (2014) 4500.

[2] S. Humez, M. Monet, F.V. Coppenolle, P. Delcourt, N. Prevarskaya, Am. J. Physiol.: Cell Physiol 287 (2004) 1733.

[3] A.L. Edinger, C.B. Thompson, Curr. Opin. Cell Biol 16 (2004) 663.

[4] A.C. Johansson, H. Appelqvist, C. Nilsson, K. Kagedal, K. Roberg, K. Ollinger, Apoptosis 15(2010) 527.

[5] X. Zhang, S.Y. Jing, S.Y. Huang, X.W. Zhou, J.M. Bai, B.X. Zhao, Sens. Actuators, B 206 (2015) 663.

[6] Z.Q. Hu, M. Li, M.D. Liu, W.M. Zhuang, G.K. Li, Dyes Pigments 96 (2013) 71.

[7] E. Liang , P.C. Liu, S. Dinh, Int. J. Pharm 338 (2007) 104.

[8] J.Y. Han, K. Burgess, Chem. Rev. 110 (2010) 2709.

[9] P. Gameiro, S. Reis, J.L.F.C. Lima, B. Castro, Anal. Chim. Acta 405 (2000) 167.

[10] S. Maskula, J. Nyman, A. Ivaska, Talanta 52 (2000) 91.

[11] D. Ellis, R.C. Thomas, Nature 262 (1976) 224.

[12] S.J.A. Hesse, G.J.G. Ruijter, C. Dijkema, J. Visser, Biotechnology 77 (2000) 5.

[13] N. Balazs, P. Sipos, Carbohydr. Res. 342 (2007) 124.

[14] T.R.L.C. Paixão, L. Kosminsky, M. Bertotti, Sens. Actuators, B 87 (2002) 41.

[15] L.J. Liu, P. Guo, L. Chai, Q. Shi, B.H. Xu, J.P. Yuan, X.G. Wang, X.F. Shi, W.Q. Zhang, Sens. Actuators, B 194 (2014) 498.

[16] J.Y. Han, K. Burgess, Chem. Rev. 110 (2010) 2709.

[17] J.H, Wang, D. Zhang, Y.Q. Liu, P.G. Ding, C.C. Wang, Y.F. Zhao, Sens. Actuators, B 191 (2014) 344.

[18] J.T. Zhang, M. Yang, C. Li, N. Dorh, F. Xie, F.T. Luo, A. Tiwari, H.y. Liu, J. Mater. Chem. B 3 (2015) 2173

[19] F.F. Han, Y.M Xu, D.C. Jiang, Y. Qin, H. Chen, Anal. Biochem. 435 (2013) 106.

[20] M.Z. Tian, X.J. Peng, J.L. Fan, J.Y. Wang, S.G. Sun, Dyes Pigments 95 (2012) 112

[21] R.A. Gottlieb, A. Dosanjh, Proc. Natl. Acad. Sci. U.S.A 93 (1996) 3587.

[22] L.-J. Ma, W.G. Cao, J.L. Liu, D.Y. Deng, Y.Q. Wu, Y.H. Yan, L.T. Yang, Sens. Actuators, B 169 (2012) 243.

[23] M. Zhang, S.Y. Zheng, L.G. Ma. M.L. Zhao, L.F. Deng. L.T. Yang, L.-J. Ma, Spectrochim. Acta, Part A 124 (2014) 682.

[24] W. Ke, L.X. Yang, C. Zhao, H.M. Ma, Spectrochim. Acta, Part A 105 (2013) 29.

[25] A.K. Jessie, W.C. Christopher, Dyes Pigments 88 (2011) 95.

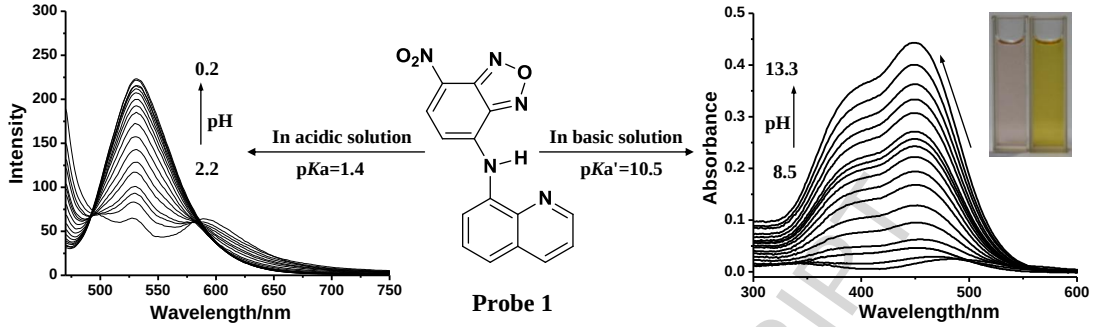
[26] F. Qian, C.L. Zhang, Y.M. Zhang, W.J. He, X. Gao, P. Hu, Z.J. Guo, J. Am. Chem. Soc. 131 (2009) 1460.

[27] p*K*a was calculated by the equation: p*K*a = pH+log[(A_{max}-A)(A-A_{min})]. see: L. Daffy, A.D. Silva, H. Gunaratne, C. Huber, P. Lynch, T. Werner, O. Wolfbe, Chem. Eur. J. 4 (1998) 1810.

[28] K.A. Alamry, N.I. Georgiev, S.A. El-Daly, L.A. Taib, V.B. Bojinov, J. Lumin. 158 (2015) 50.

[29] W. Jiang, Q. Fu, H. Fan, J. Ho, W. Wang, Angew. Chem. Int. Ed. 46 (2007) 8445.

[30] H.A. Bari Indhar, A.W.K. Khanzada, Jour. Chem. Soc. Pak. 22 (2000) 1.



Graphical abstract

A fluorescent and colorimetric pH probe, 4-(8-Quinolyl)amino-7-nitro-2,1,3-benzoxadiazole (**1**), was synthesized. Under alkaline condition, **1** with a p*K*a value 10.5 could be applied as a colorimetric probe to pH change from 8.5 to 13.3. And **1** with a p*K*a value 1.4 could be used as a fluorescent "turn-on" pH probe under strong acidic condition (pH value is from 2.2 to 0.2).

Highlights

- A new fluorescent and colorimetric pH probe (**1**) was synthesized.
- The probe could be applied as a colorimetric probe to pH change from 8.5 to 13.3.
- The probe could be used as a fluorescent "turn-on" pH probe with pH range from 2.2 to 0.2.